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Development of a Polymeric Cementing and Encapsulating Process for Managing Hazardous Wastes

TRW Systems Group, Redondo Beach, Calif

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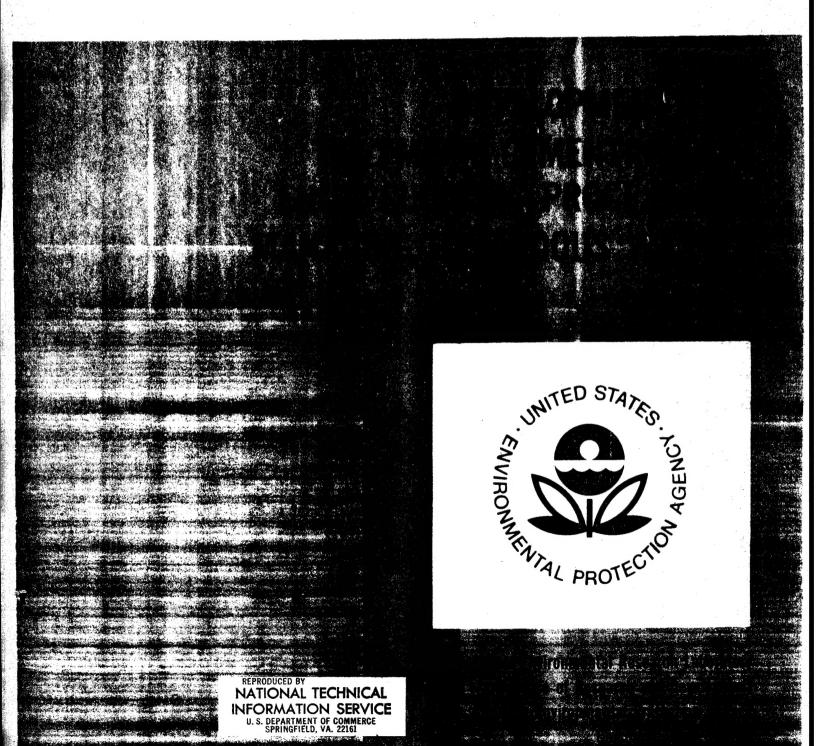
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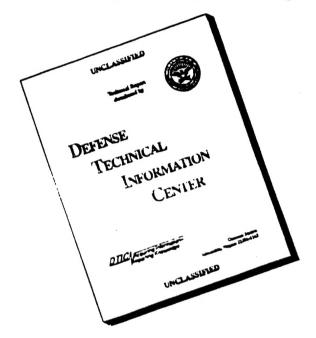
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A process using polymeric materials to cement and encapsulate dry hazardous waste was researched, developed, and evaluated. The process involves cementing particulates of waste into 500 to 1000 pound agglomerates, and then fusing a plastic jacket onto the agglomerate surfaces, thereby encapsulating them. Polybutadiene, as a binder resin, was found to be capable of cementing waste 94 to 96 percent by ready processing of the agglomerates. Encapsulating the waste-binder agglomerates with 1/4-inch jacket of high density polyerthylene can be carried out by packing powdered polyethylene about the agglomerate and then fusing the powder in situ. method was satisfactorily applied to produce laboratory specimens containing, in some cases, high concentrations of highly water soluble heavy metal wastes, e.g., sodium metaarsenate. Test specimens were subjected to leaching solutions for 120 days and mechanical stresses to evaluate the processes' capability to isolate the hazardous waste from selected disposal environments. Results indicate the processes' ability to prevent, or limit to acceptable levels, the release or delocalization of the hazardous waste to the environment under various disposal schemes. This report discusses the process and provides results of the evaluations.

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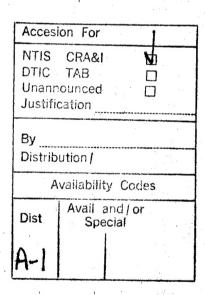
# DEVELOPMENT OF A POLYMERIC CEMENTING AND ENCAPSULATING PROCESS FOR MANAGING HAZARDOUS WASTES

by

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#### **FOREWORD**

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare fo the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communication link between the researcher and the user community.

This report provides results of research and evaluation of a process for managing wastes hazardous to man, other life, and to the environment. Efforts were concentrated on providing a treatment method for hazardous wastes for which available techniques were not adequate to prevent environmental damage during disposal.

#### **ABSTRACT**

This report provides method, materials, evaluations and engineering for managing wastes hazardous to man and other life by localization employing an organic, polymeric cementing and encapsulating process (TRW process). Specimens, of cubic dimensions three inches on edge, consisting of wastes cemented with 3 to 4% by weight polybutadiene binder and encapsulated by 1/4 inch polyethylene jackets, were fabricated with selected wastes and subjected to exacting leaching conditions and mechanical testing. They were found to exhibit excellent retention of contaminants in leaching by a broad spectrum of aqueous solutions and to withstand degradation under high compressive and impact mechanical forces.

Engineering study yielded a process flow diagram, a product design, and examined process economics parametrically. The former included a potential plant design and mass and energy balances. Cost effective products were characterized as follows: dimensions, cubic, approximately two feet on edge; weight, in the range 800 to 1000 pounds; jacket, about 1/4 inch thick polyethylene resin; encapsulated hazardous waste agglomerate cemented by 3% w/w polyethylene resin and jacketed by 4% w/w polyethylene resin. The cost of waste passivation was estimated at \$91 per ton at 20,000 tons per year throughput. The parametric study related cost to various parameters and indicated that the most cost sensitive area was cost of resins, accounting for approximately 50% of the total cost.

There is a spectrum of difficult to manage hazardous waste for which the TRW process of agglomeration and polymeric encapsulation appears to be uniquely applicable. Specific examples of such wastes are: some wastes contain contaminating compounds in the form of alkali metal salts, e.g., sodium metaarsenate, that resist "fixation" by resins (inorganic as well as organic) and may be readily dispersed by dissolution from resin localized waste (unencapsulated) into the ecology. Others contain non-soluble compounds such as arsenic trisulfide which may be disseminated by physical dispersion. In addition, unencapsulated wastes localized satisfactorily

by resins under certain conditions may, however, maintain resistance to delocalization over a range of environmental conditions more limited than that realizable by encapsulation.

This report is submitted in fulfillment of Contract No. 68-03-2037 under the sponsorship of the Environmental Protection Agency. Work was completed in July 1975.

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### 1. INTRODUCTION

Under Section 212 of the Resource Recovery Act of 1970, the Environmental Protection Agency was charged with the preparation of a Report to Congress defining and describing various aspects of hazardous waste management. Of particular concern are those wastes which possess the potential of harm to man and/or the environment. The hazardous wastes may be either in the solid state or mixed with a liquid, most often water, in the form of sludges, slurries or slimes. Almost any branch of modern industry, metallurgical, chemical, ceramic, mineral, food processing, metal treatment, petroleum refining, treatment of municipal sewage, etc., leaves behind some kind of wastes; described varyingly as tailings, scraps, rubble, garbage, refuse, residue, sludge, slime, slurry, mud, etc. These wastes often contain toxic compounds including arsenic, lead, mercury, selenium, beryllium, cadminum, zinc, and chromium. The potential hazard is increasing rapidly due to the greater quantities of concentrated toxic solids and sludges being produced by policies and equipment designed to limit air and water pollution.

The Report to Congress was based upon specific contract efforts designed and programmed to provide information and insight necessary to the presentation of a complete and accurate picture. The first contract effort, initiated in July 1971, identified a number of hazardous materials, their sources and quantities, and the technology utilized for their treatment. The second contract effort, initiated by TRW in December 1971, had three concurrent objectives: (1) refine the listing of hazardous wastes based on further information, (2) analyze and assess current hazardous waste disposal technology, and (3) define research and development necessary to provide information or adequate technology. This effort culminated in a final report delivered in February 1973.

The TRW work indicated that among the areas of application used in waste elimination, Figure 1, the one pertaining to elimination of non-destructible wastes (localization) in particular required extra emphasis in additional development. Certain wastes contain hazardous, heavy metals,

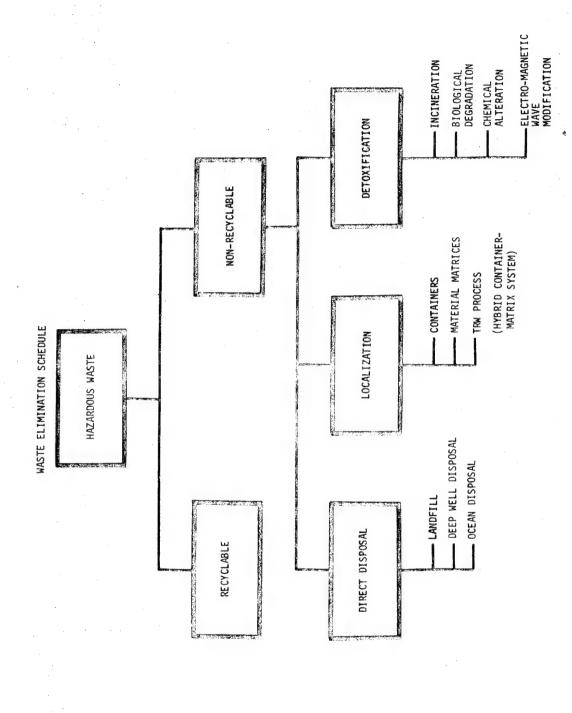


Figure 1. Areas of Application

e.g., arsenic, lead, mercury, selenium, beryllium, cadmium, zinc, and chromium, others contain fluorides, bromides and iodides, which can be controlled only by localizing the materials, or isolating and then localizing the contaminants. Present containerization and matrix incorporation methods that were employed did not assure high performance localization. Successful localization signifies that the probable release of toxic materials from localized waste solids and sludges is at a level consistent with both short-term and long-term environmental protection.

In July of 1973, the scope of the TRW study was expanded to include initial bench-scale process development efforts with the objective of demonstrating the feasibility of a new toxic waste localization process (TRW process, Hybrid Container - Matrix System).\* In the process, dry wastes are agglomerated by cements which yield stiff, strong composites with very high waste contents. Subsequently, the agglomerates are encapsulated by jackets of selected materials. These jackets are designed to adhere to the surface of the agglomerate and to exhibit mechanical advantages as well as the desired chemical ones.

Wastes localized in this fashion were assessed to consume minimal amounts of "fixing" material and yet withstand more effectively than current localization methods the mechanical and chemical stresses of various disposal schemes, such as landfill, deep well disposal, and ocean disposal or alternative management for sufficient periods of time to ensure safety and protection. Thus, wastes localized by the TRW process were expected to exhibit load bearing properties in advance of those characterized by containers with non-agglomerated contents. The products of the new process, however, retain the singular advantage of containers by providing a distinct material discontinuity at the interface of the waste and the environmental stresses. In the non-containerization method, localization of wastes into material matrices, such as blending wastes into molten resins followed by solidification of the melt, leaves unprotected wastes at the interface subject to delocalization by water leaching and other dispersion forces. As increasing concentration of wastes are localized in material matrices in order to conserve the amount of "fixing" material employed, performance properties are compromised due to

<sup>\*</sup>See Section 3.1 for detailed description of concept of TRW process.

increasing concentration of waste exposed to environmental stresses. With delocalization of surface exposed waste, more waste is exposed due to the resulting increased surface area; delocalization then proceeds into the body of the product.

The initial phase of the TRW process development program under Contract No. 68-03-0089 to the Solid and Hazardous Waste Research Laboratory of the National Environmental Research Center, Cincinnati, Ohio, was designed to determine information on three important process characteristics: (1) the technical behavior of agglomeration and encapsulation; (2) the ability of the method to passivate hazardous wastes; and (3) the process economics. In this program waste simulants were used to ease the handling problems and to insure a known baseline for the processing and environmental tests. A number of different organic and inorganic cements and jacketing substances were investigated in various proportions in order to identify suitable materials. The effectiveness of waste localization was determined on the basis of leach tests using various solutions in which passivated waste blocks were immersed. A preliminary design and economic analysis was determined for both the organic and inorganic cementation processes based on the process data developed in the laboratory. This effort culminated in a final report delivered in November 1974.

Organic cements were favored over inorganic ones, such as Portland Cement and Plastor of Paris, because they were found to cure more rapidly and to "fix" higher concentrations of waste. Details concerning organic cementation is given in Appendix A. A feature of this work was the identification of a resin binder system which agglomerated high concentration of hazardous waste, and two resins that readily encapsulated the agglomerates with tough, high performance jackets. The binder system was based upon carboxyl terminated oligomers of 1,2 polybutadiene and epoxide chain extenders. It was found to stabilize dry, particulated waste in concentrations as great as 96 to 97% by weight. The resulting aggregates of waste were dimensionally stable and strong in compression. They were readily encapsulated by 1/4 inch jackets employing polyvinyl chloride plastisols and powdered polyethylene. These jacketing resins, particularly the latter, are mechanically tough and chemically stable, and were found to undergo upon processing minimal penetration into the agglomerate. This

made the jackets more effective as barriers by allowing the bulk of the resins, about 1/4 inch thick, to concentrate upon the surface, yet there was sufficient penetration to provide desirable mechanical locking of the jacket to the substrate. The above and other features, such as the realization of high performance products, coupled with the ease of the processing, indicated that the TRW process was a cost effective means for hazardous waste localization.

This report provides the results of additional study for the Solid and Hazardous Waste Research Laboratory on the localization of wastes containing heavy metals by employing organic resins for formation of heavy metal waste agglomerates and for jacketing the agglomerates. Based upon the results of the previous study, cost effective, high performance resins selected for employment on this work were polybutadiene for agglomerate formation and high density polyethylene for jacketing the agglomerates. The three major objectives of this work were: (1) to show general applicability of the above resins in the TRW process to passivation of dry, heavy metal wastes notwithstanding their chemical compositions and material consistencies, and provide an encapsulation method suitable for large scale operations, (2) to demonstrate the high performance character of the products under exacting environmental stresses, and (3) to provide initial process designs and cost estimates for localization of wastes.

This report is set forth as follows: Section 2 provides the selection, identification, and characterization of wastes for localization by the TRW process. In Section 3, demonstration is provided with respect to general applicability of the passivation process; the laboratory method, developed and employed for localizing wastes, is given in detail. Section 4 shows the results of leaching localized waste products by a broad and exacting series of aqueous leaching solutions. The mechanical characterization of products is given in Section 5. Section 6 shows process designs, the general process economics model, and the determined costs for localizing wastes. In Section 7, industrial wastes are analyzed with respect to localization by the TRW process. Section 8 gives generalizations of and potential modifications to the accomplished work.

# 2. IDENTIFICATION, SELECTION, AND CHARACTERIZATION OF WASTE STREAMS

The major thrust of this portion of the work was to identify hazardous, heavy metal containing wastes with broadly varying chemical compositions and material consistencies for localization by the TRW process. Such wastes were required in order to demonstrate viability of the premise that the TRW process is applicable to dry wastes generally without need for tailoring the process to the specific waste. (Waste types are discussed in Sections 7 and 8.) With this objective in view, the selection of waste was geared to those constituting the largest output from industrial sources. The selection criteria, however, were compromised in certain cases because some wastes could not be made available for investigation within the time scope of the program.

The characterization of wastes was limited mainly to information offered by the suppliers. The chemical compositional makeup of some wastes employed in preparing test specimens, however, were assayed; the results are provided in Section 4, Leaching Tests.

#### 2.1 WASTE IDENTIFICATION

Two types of wastes were sought for evaluation in the TRW process:

- One characterizing composition of heavy metal contaminants issued by chemical industry and waste sequestering operations.
- Another characterizing composition soluble in water wherein soluble salts are laced by small concentrations of heavy metal.

The former can be viewed as product of heavy industry while the latter stems from fine industry such as pesticide production. The latter material will also test the performance of the TRW process in passivation of contaminants such as salts of fluorides, cyanides and bromides.

The U.S. Army Corps of Engineers, Vicksburg Experimental Station supplied to this study ten waste sludges of the first type. The sources of the wastes and the major contaminants in their contents are indicated in Table 1.

Additional sludges were sought from other sources, but those received (described below) were not used because they were similar to Waterways electroplating and pigment production sludges.

Electroplating sludge, consisting of 5 gallons of a liquid containing less than 1% solids, was obtained from Ajax Hardware in the City of Industry, California. The major contaminants were zinc, copper and cyanide. U.S. totals of electroplating wastes produced each year includes 2 million pounds of copper and 21 million pounds of cyanide.\* It is our understanding that these wastes normally are disposed of through the sewer systems.

Paint sludges were provided by Sinclair Paint Company of Los Angeles in two forms, water-based and organic solvent. The major contaminants in the water-based sludge sample, which stem from the production of enamels, were chromium and mercury. The U.S. production total for this type of sludge is 26 million pounds per year.\* The second sample received from Sinclair Paints was solvent-based sludge from flat vinyl paint production. The major contaminants were lead, chromium, cadmium and cyanide. The paint industry produces 36 million pounds per year of this type of sludge.\* Both forms of sludge are usually disposed at sanitary landfills in 55 gallon drums.\*

Concerning the latter type waste, monosodium methanearsonate containing waste was obtained from operations of the Ansul Chemical Company in Marinette, Wisconsin. Other identified wastes contained cacodylic acid and sodium cacodylate, but the monosodium methanearsonate waste was more

TRW Report #21485-6013-RU-00 prepared for the Environmental Protection Agency, Recommended Methods for Reduciton, Neutralization, Recovery or Disposal of Hazardous Wastes, Volume XIV.

# TABLE 1. WATERMAYS WASTES

Code No.	Source	Major Contaminants
001	$\mathrm{SO}_{\mathrm{X}}$ scrubber sludge, lime process, eastern coal	ca, $50_4^{=}/50_3^{=}$
200	Electroplating sludge	Cu, Cr, Zn
S	Nickel - Cadmium berteny production sludge	Ni, Cd
400	$\mathrm{SO}_{\mathrm{X}}$ scrubber sludge, limestone process eastern coal	cu, so <sub>4</sub> /so <sub>3</sub>
200	$\mathrm{SO}_{\times}$ scrubber sludge, double alkali process, eastern coal	Ma, Ca, ${\rm SO_4}^{=}/{\rm SO_3}^{=}$
009	$\mathrm{SO}_{\mathrm{X}}$ scrubber sludge, limestone process, western coal	ca, so <sub>4</sub> /so <sub>3</sub>
700	Pigment production sludge	Cr. Fe, CN
800	Chlorine production brine sludge	Na, Cl_, Hg
006	Calcium fluoride sludge	Ca, F
1000	$\mathrm{S0}_{\mathrm{x}}$ scrubber sludge, double alkali process,	$cu, Na, SO_4 = /SO_3 =$
	western coal	

prevalent. Since the above compounds come from one industry, pesticide manufacturing, it was decided to sample the waste produced in larger quantities. The waste sample contained 1-1/2% by weight monosodium methanearsonate, 49% sodium chloride and 49% sodium sulfate. Such arsenic containing wastes are presently stored on-site at Ansul in concrete vaults.

Arsenic trioxide containing waste is recovered in large amounts from the flue dust of metal smelting operations. Many smelters send this waste to American Smelting & Refining Company (ASARCO) in Tacoma, Washington. After recovering metals of value, ASARCO has been storing the arsenic trioxide. Presently, the compound is recycled to industry. Since ASARCO ships only in carload lots, it was not practical to obtain this material in sample quanities.

#### 2.2 SELECTION

The wastes selected for agglomeration study, Section 3.2, were those designated in Table 1 as 200, 300, 500, 700, and 900. These materials differ significantly in chemical composition and material consistency. Furthermore, they stem from a broad spectrum of sources in the chemical industry, each source issuing significant quantities of waste. A blend of equal parts by weight of 200, 300, 500, 700, 800, and 900 were employed in encapsulation of wastes, Section 3.3, and for detailed leaching and mechanical property studies, Sections 4 and 5. The blend contained the following atoms: Cu, Cr, Zn, Ni, Cd, Na, Ca, Fe, Hg.

The waste with monosodium methanearsonate was also selected for encapsulation and study. The arsenic contaminant, existing as a sodium salt in a mixture of sodium salt compounds, is expected to be very water soluble. As such, specimens from this material for aqueous leaching studies would provide an exacting test of the ability of the encapsulation method to passivate such wastes. Passivated sodium chloride was also studied, thereby gaining some insight of the ability of the TRW process to passivate alkali metal cyanides, fluorides, and similar compounds.

# 2.3 CHARACTERIZATION

Five gallon quantities of aqueous sludges 200, 300, 500, 700, 800 and 900 were dewatered to a consistency that exhibited no mobile water by exposing the material to the atmosphere and sunlight. The resulting residues were then heated in an oven at 300°F for about 1/2 hour. The residues thereafter granulated readily with mechanical stirring. A uniform consistency, i.e., absence of gross aggregates, was sought in particulation. No attempt was made to obtain a particular particle grind because various material consistencies were desired for agglomeration and encapsulation. Demonstrating successful passivation would indicate that it is not necessary to reduce wastes with different particulation characteristics to a specific grind, nor is it necessary to reduce a given waste repeatedly to the same grind. In some cases, mechanical stirring was not necessary. Residues of sludges 500 and 900 did not require stirring to obtain uniform material consistencies suitable for encapsulation.

The following two figures show the particulated residues of 200 and 700 under 100 times magnification.

The residues appeared as agglomerated fines. The average dimensions of the agglomerates ranged between 5 to 15 mils. Sparkle exists in Figure 3 and it is not evident in Figure 2. This may be due to highly reflecting surfaces; such ordered surfaces characterize crystal faces. It appears that crystals of such magnitude may be absent in sludge 200 residue.

With respect to the monosodium methanearsonate containing waste, it was grey-white in color and exhibited the consistency of sugar. As a sodium chloride source for this work, table salt was employed.

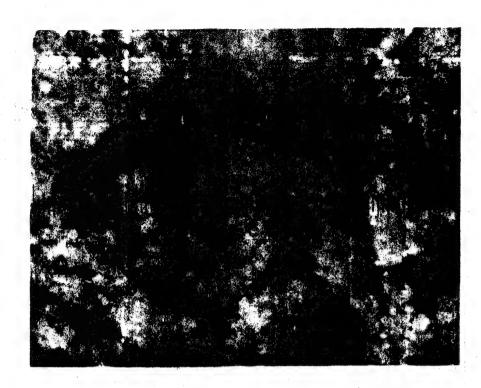


Figure 2. Waste 200 Residue (Electroplating Sludge)
Magnification 100X, Scale Division 0.5 Mil



Figure 3. Waste 700 Residue (Pigment Production Sludge)
Magnification 100X, Scale Division 0.5 Mil

#### 3. APPLICATION OF LOCALIZATION PROCESS TO SELECTED WASTES STREAMS

The resins employed for localization of wastes described in Section 2.2 were modified polybutadiene and polyethylene. Their selection resulted from earlier work under Contract No. 63-03-0089. The modified polybutadiene resin for waste agglomeration was assessed to provide the following advantages: blends readily with and contains large quantities of heavy metal wastes; remains shelf stable; agglomerates wastes by fast chemical reaction that is not sensitive to waste composition; yields tough agglomerates, augments dewetting from mold; provides chemical sites for desirable interaction with jacketing resin; and fashions readily from butadiene, a commodity used for making rubber for tires. The jacketing resin, high density polyethylene, was expected to show the following advantages: excellent chemical stability, nonbiogradable, tough and nonpermeable to metal ions and other waste permeants, functional over a wide temperature range, low cost, and commercially available in pulverized form allowing for ready envelopment of agglomerated wastes with resin jackets.

The bove resins in combination were assessed to yield high performance, cost effective passivated waste products. This assessment could not be applied distinctly to other resin systems, consequently, the polybutadiene polyethylene resin systems are unique, in our opinion, for fabricating passivated wastes by agglomeration and encapsulation. Included in the assessment were product processing techniques. Technological barriers to ready reproducible processing of encapsulated wastes are, in our opinion, markedly reduced by the physical and chemical character of these resins.

Employing the above resins, the major thrust of this portion of the work was to demonstrate and realize the following:

 The general applicablity of the TRW process to localization of dry, heavy metal wastes without need for process modification.

- A method for agglomerating and encapsulating wastes that can be readily carried out and yields products with seam free resin jackets adhering tenaciously to the waste agglomerate.
- A set of specimens for laboratory testing to demonstrate the performance capabilities of the passivated wastes.

#### 3.1 PROCESS CONCEPT

Prior to providing in the following sections the experimental work of this study, the process concept and the attendant advantages are outlined here. The thrust of the experimental work is to provide proof that the anticipated advantages are readily realizable.

In the TRW process, unconfined particulate waste is first agglomerated and a container is then fabricated about it, thus yielding an encapsulated product. Conventionally, particulate waste is entered into a container and the waste is sealed by fixing a lid onto the receptacle. In effect the TRW process is the reverse of the conventional process, and this gives rise to a very significant benefit: in the event the product is subject to an applied mechanical load, such as that stemming from overburden in a landfill or from stacking products in transporting, that load is sustained by the product contents rather than the product walls. Since the walls need not be structured to be load bearing, an increased number of types of material are thus made suitable for encapsulating waste. Most importantly. it makes possible the use of softer materials such as plastics in the fabrication of high performance products rather than hard, stiff metallic ones. As a class, it is well recognized that plastics are more resistant to chemical corrosion than metals. With cost considerations, plastics have no metallic counterparts vis-a-vis chemical stability.

Another important advantage of the TRW process in contrast to conventional containers concerns the nature of sealing the waste content. Fixing a lid onto a receptacle in order to effect a proper seal usually

involves the use of materials different than those employed in receptacle and lid fabrication. These materials are usually gaskets, o-rings, sealants etc. The use of dissimilar materials requires skill in their utilization for effecting proper closure. Even then, containers are usually observed to fail at the juncture of receptacle and lid. However in the TRW process, a single material is employed for encapsulation of wastes and the product is characterized by being seam free.

With anticipated performance advantages characterizing an agglomerated waste encapsulated seam free by plastic, it remains to select the specific plastic: one that is low cost, readily processable, mechanically tough and chemically resistant to both the chemical action of the agglomerate and the disposal environment. Under Contract No. 68-03-0089 the preferred resins were found to be polyvinyl chloride plastisols and powdered polyehtylene. Since plasticizers are employed in the manufacture of the plastisols, and these are potentially leachable from the plastic, the choice was narrowed to powdered polyethylene. Of particular importance in the choice of this polyolefin was the commercial availability of its powdered form from several large plastic producers. It is very desirable to utilize the powder because it makes possible ready fabrication of thick elements of plastic onto agglomerates without need for heavy duty equipment by the novel means to be described later. With thick elements, one gains mechanical advantages as well as the expected chemical ones. This realization of thick coatings upon substrates is not readily attainable through the art of coatings technology.

The desired product of the TRW process should consist of a tough, chemically stable plastic jacket encapsulating an agglomerate of waste and furthermore tenaciously adhering to its surface. A product with a properly adhered plastic jacket is expected to exhibit greater resistance to mechanical stresses than one not so characterized. In the former case, the substrate reinforces the plastic, for examples, with respect to resisting puncture, abrasion, and mechanical impact. Without this reinforcement, the plastic per se must withstand the mechanical stress thus giving rise to products of lessor performance.

Up to this point, the advantages are presented concerning a product. characterized by a resinous jacket encapsulating and adhering to an agglomerated waste. Attention must be given now to the nature of the agglomerated waste in order to realize ease of processing and high performance products. It is desirable for particulate waste to be treated with resin for subsequent cementing without employing heavy duty equipment. It is necessary for the treated material to be shelf stable. (Thus the agglomerating steps can be carried out at ones convenience rather than in adherence to a given time schedule, a constraint that arises in use of shelf unstable material. Specified time intervals between process steps i.e., resin coating the waste particulates followed by cementing them together, limits the flexibility of the agglomerating operation.) It is obviously advantageous to have agglomeration occur rapidly upon its initiation. During the agglomeration, it is important for the waste particulates not to settle out but remain homogeneously dispersed in the agglomerate in order to realize optimal mechanical properties. And to reduce cost, the resin employed for waste particulate agglomeration must be capable of stabilizing a high content of waste.

The resin system selected for cementing waste particulates into agglomerates was based upon 1.2-polybutadiene. This material is readily prepared in polar organic solvents by elemental sodium polymerization of butadiene, a well known material in making of synthetic rubber. Sodium not only causes butadiene polymerization, but in addition allows the positioning of chemically functional groups at the terminal ends of the polybutadiene chain. (The nature and role of the functional groups will be discussed later.) It is pointed out here that the 1,2 configuration is considered to be important for the purposes of this study mainly because it is inherently stabile in air. Other configurations of polybutadiene such as 1,4 cis and trans do not exhibit this advantage. The later materials unstabilized, will oxidize readily when exposed to air. In commercial practice the cis configuration, which is very important in truck tire manufacture, is stabilized with antioxidants. Such stabilization is not suitable when polybutadiene is geared for use as a cement for rapidly fabricating a stiff product because the high degree of chemical condensation required quickly would not be readily realizable when it is carried out in the presence of antioxidants. Antioxidants interfer with the condensation reaction. Thus the stability in air of 1,2 not only yields shelf stable resin coated waste particulates but also ones that chemically condense readily.

The chemical condensation of 1,2 occurs with peroxide initiation. The required peroxides are well known in rubber vulcanization technology and are commonly employed and commercially available. The use of the peroxides, however, requires an elevated temperature (about 320°F) in order to initiate chemical condensation. Unfortunately, upon heating a mixture of particulates with 1,2-polybutadiene resin, the resin becomes fluid and the particulates then tend to settle out. In order to preclude such an event the functional groups of the polymer is invoked.

The functional groups are geared to react with a chain extender that is added to the cement formulation of resin and peroxide at temperatures lower than 320°F. This reaction increases the viscosity of the resin mixture thus counteracting the thermally induced fluidity. Under these circumstances, the particulates are expected to remain fixed and homogeneously dispersed in the resulting agglomerate. Such properties, and the nonpolar nature of 1,2-polybutadiena, allow incorporation of high concentrations of waste into the resin cement with minimal sacrifice of performance. The technical advantages given above, shelf stability, fast reactivity, high solid content, coupled with the desirable ready demolding character of polybutadiene products and low cost cannot, in our opinion, be duplicated in any other organic cement.

The preferred functional groups are carboxyl ones. These are readily fixed to 1,2-polybutadiene by blowing carbon dioxide into reaction vessel after the sodium induced polymerization of butadiene has taken place followed by acid neutralization. The resin is isolated if desired upon vaporization of the solvent. (Although the isolated resin was used in this work because it was available in this form from the vendor, use of the isolated resin is not required, nor indeed desirable from a cost viewpoint. In practice, the

polymerization solution is expected to be treated with peroxide and chain extenders and then employed as such to wet hazardous waste particulates. The solvent will exhibit the property of being readily vaporizable, it will be condensed and then reemployed for additional polymerization.) The preferred chain extenders are epoxides, particularly the well known and most commonly employed one, the diglycidyl ether of bis phenol A.

It is pointed out here that all the materials except for the 1,2 polymer employed in the stabilization of hazardous waste stem from large scale commercial operations. Indeed it is the objective of this study to employ only prevalent low cost materials. The 1,2-polybutadiene polymer with terminal carboxyl groups is not available generally in the U.S., the material is made commercially at the present time in Japan, but the art is well known and the preparation easily carried out. The major expense in preparing commercial 1,2-polybutadiene lies in purification of the material, that generally involves freeing the material from the products of acid neutralization, which is required because it is geared for electrical and coatings use. For the purpose of cementing waste such a pure material is not necessary (although employed here because it was available) and a crude polymer, in our opinion, will serve equally well.

The TRW process, although employing well known materials, employes them in unique combination. This combination is geared to yield products having high performance yet requiring minimal amounts of material in their fabrication. (The materials per se are of the lowest cost consistent with realization of high performance.) It is estimated that total resin required will be about 7 to 8% w/w with 3 to 4% employed in cementing about 4% employed in encapsulating the resulting agglomerates.

The fabrication of products is readily carried out. Particularly advantageous, no heavy duty equipment is required. The process is geared to be carried out by unskilled workmen and it does not require adherence to a strict routine.

#### 3.2 GENERAL APPLICABILITY

Residues of dewatered Wasterway sludges 200, 300, 500, 700, and 900, isolated as described in Section 2.3, were selected for demonstrating general applicability of the waste passivation process. They were coated by an acetone solution of modified polybutadiene. The solution was combined with about 160 grams of residue and mechanically stirred in a two gallon Hobart mixer. This blending operation required five minutes. After blending, a constant weight material was obtained in about two hours by leaving the material exposed to the atmosphere. The resin content of the grind was about 4% by weight.

Prior to agglomerating the resin coated particulated wastes, it was considered important to observe the free flowing character of the particulates and their shelf stability. Free flowing particulates facilitate loading of large molds for subsequent thermal fusion of particulates into large agglomerates.\* The property of shelf stability places essentially no time constraints upon initiating fusion operations. These advantages contribute to ease of making passivated products. The product performance is consequently less sensitive to the mechanics of product fabrication.

Agglomeration of the particulates was carried out under moderate mechanical pressures in the temperature range of 250 to 400°F and at various time intervals after the resin coating operation. The details of agglomeration and encapsulation are provided in Section 3.3. Here demonstrations were sought which showed different wastes readily agglomerating over a wide temperature range from free flowing resin coated waste particulates stored at various time intervals.

Determination of size of cost effective, passivated wastes is given in Section 6.1.1, Determination of Dimensional Nature of Products.

The following figures show samples of resin coated wastes 200, 300, 500, 700, and 900 as free flowing particulates and fused agglomerates. The coated particulates flowed readily through the stem of a glass funnel, Figures 4, 6, 8, and 10. No residue was noticed on the funnels after flowing the samples. Figure 12 exhibits the discrete nature of the particulates. In the above operations, and after storing in containers, the particulates remained discrete and free flowing.

The agglomerated particulates, Figures 5, 7, 9, 11 and 13, yielded hard, tough specimens, some exhibiting a glossy finish. Agglomeration was carried out on resin coated particulates after time intervals of five minutes to thirty days. All the specimens showed hardness values greater than Shore A 100.

This work verified the premise that highly loaded agglomerates can be fashioned from different wastes over a wide temperature range, and that resin coated wastes can exist as free flowing particulates which exhibit shelf stable properties.

# 3.3 METHOD OF WASTE AGGLOMERATING AND ENCAPSULATING

The purpose of this element of work was: (1) to establish an agglomeration and encapsulation method that could form a basis for large scale production of agglomerated wastes weighing 500 to 1500 pounds with one-fourth inch thick resin jackets,\* and (2) to fabricate specimens to demonstrate the performance capabilities of the passivated wastes. The specimens for testing were fabricated as cubes 3 inches on edge, characterized by a

Rationale for size of passivated waste products is given in Section 6.1.1, Determination of the Dimensional Nature of Products.

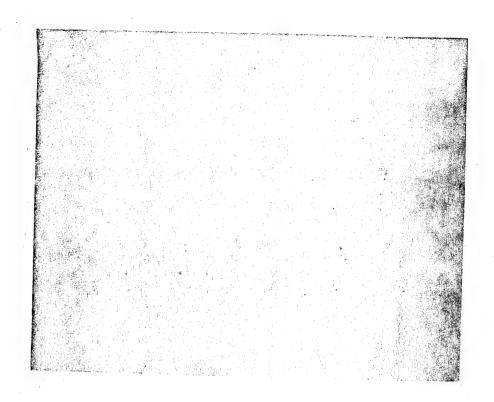


Figure 4. Polybutadiene Coated Residue of Sludge 200

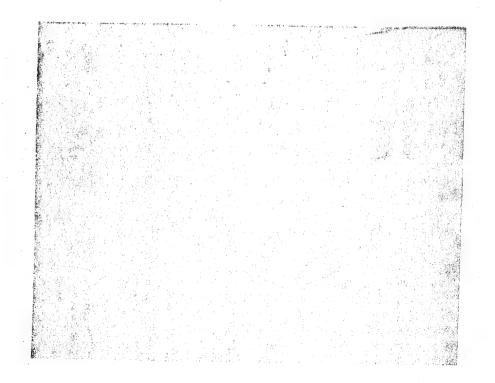


Figure 5. Fused Residue of Sludge 200

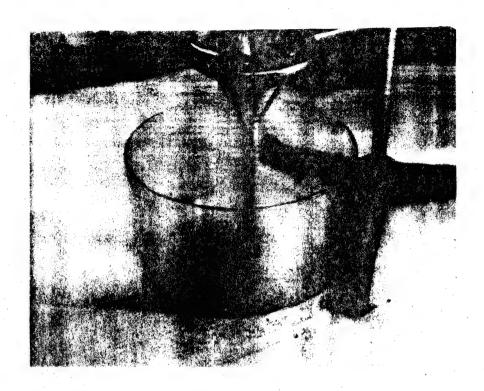


Figure 6. Polybutadiene Coated Residue of Sludge 300

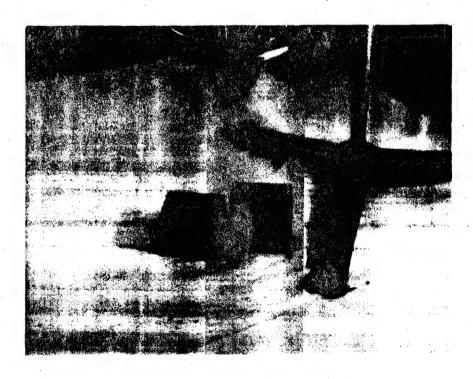


Figure 7. Residue of Sludge 300 Fused at 310°F

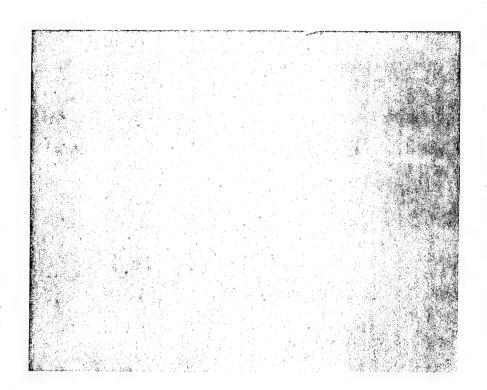


Figure 8. Polybutadiene Coated Residue of Sludge 500

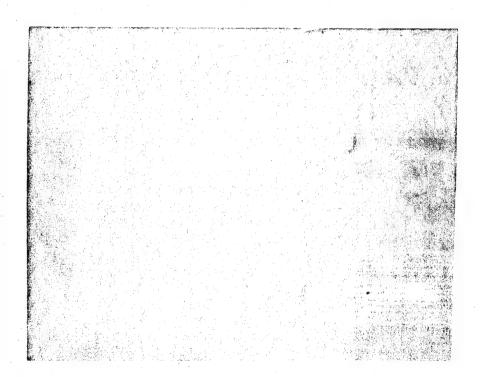


Figure 9. Fused Residue of Sludge 500



Figure 10. Polybutadiene Coated Residue of Sludge 700



Figure 11. Fused Residue of Sludge 700



Figure 12. Polybutadiene Coated Residue of Sludge 900

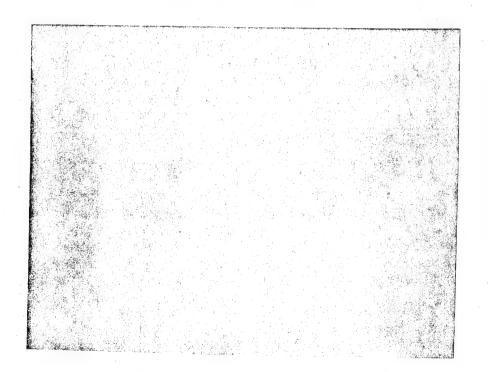


Figure 13. Fused Residue of Sludge 900

1/4 inch thick resin jacket adhering to a cubic agglomerate of waste, 2-1/2 inches on edge. The densities of the agglomerate wastes depended upon the nature of the materials. Agglomerated particulates of residues of 200 and 300 with 4% by weight binder were determined to be 98  $1b/ft^3$  and  $110 \ 1b/ft^3$ . A working value of  $100 \ 1b/ft^3$  was employed for estimating dimensions of large passivated waste products.

The passivated waste products must be characterized by seam-free, encapsulating resin jackets, and by tenacious adhesion of jacket to agglomerate in order to realize high performance products. Seam-free jackets were readily fabricated according to the method given below. Tenacious adhesion of jacket to agglomerate occurred in all cases due to an incremental penetration of the jacketing resin into the agglomerate, which formed a mechanical lock between jacket and agglomerate. Although chemical adhesion between jacket and agglomerate binder was also expected to occur due to the chemical nature of the adherends, it was not possible to assess the respective contributions of the mechanical lock and the chemical bond to the strength of the adhesive bond.

The method of agglomeration and encapsulation, utilizing the blend of sludge residues described in Section 2.2, is provided here in a pictorial sequence. The encapsulated products are shown in cross section.

# 3.3.1 Procedure for Passivation of Wastes

Figure 14 shows the agglomerated waste blend emerging after molding. The agglomerate slipped readily from the mold even though it contained high solid loadings, i.e., about 95% by weight wastes. Facile mold release can be attributed to the non-polar chemical nature of polybutadiene and to agglomerate contraction from shrinkage of the material while undergoing a thermosetting reaction and subsequent cooling. In some cases, however, slippage did not occur readily. Further exploratory work showed that 0.1% by weight powdered polyethylene incorporated into the agglomerate would enhance slippage in all cases. With respect to molding 500 to 1500 pound agglomerates, the agglomerates would be removed by slipping the mold upward as described in Section 6 rather than by extracting the agglomerate from the mold as shown in Figure 14.



Figure 14. Agglomerated Hazardous Waste Residue Emerging from Mold

In Figure 15 the agglomerate is shown positioned for resin jacketing; Figure 16 shows the agglomerate submarged in powdered polyethylene.

Figures 17 and 18 show the five-sided resin jacketed agglomerate after being removed from its mold upon completion of thermal fusion of the powdered resin at 350°F followed by solidification of the melt.

An indented configuration was selected in the design of the mold because it secured the agglomerate during the five-sided jacketing step. The figures show a "step" in the jacket at the "lips". In addition, when the final jacketing step was carried out, the step of solidified polyethylene contributed to faster penetration of heat at the lips than at other points. Thus, the added powdered polyethylene at the lips melted first thereby allowing displacement of entrapped air upward and through the non-fused material. By this method, seam-free fusion was readily carried out.

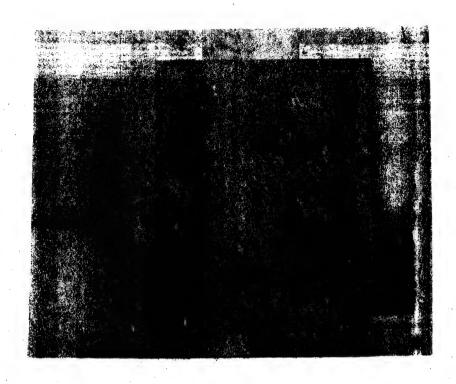


Figure 15. Hazardous Waste Agglomerate Positioned for Resin Jacketing

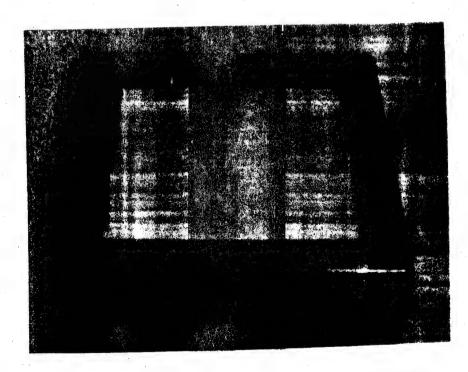


Figure 16. Agglomerate Submerged in Powdered Polyethylene

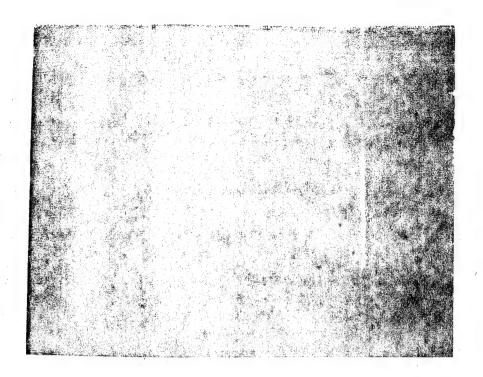


Figure 17. Non-Jacketed Side Seen on the Free-Standing Agglomerate After the First Jacketing Step

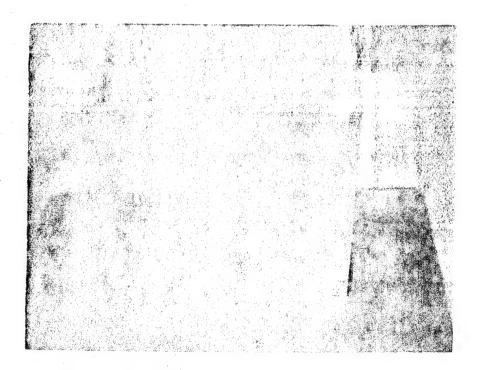


Figure 18. Five-Side Jacketed Agglomerate Resting on Mold Pedestal

Particular attention was given in this work element to understanding the process for introducing the resin for agglomerate jacketing. In the laboratory operation, the powdered resin was hand packed into the cavity; this procedure would be cumbersome and possibly costly in a production operation. With respect to jacketing 500 to 1500 pound blocks of agglomerate, a powdered resin would be sucked into the area between the mold and the agglomerate with a vacuum system. The resin would then be fused onto the agglomerate by heating through the mold. As presently visualized, a port would be provided at the bottom of the mold shown in Figure 15 and a vacuum line would be attached. A cover plate with port for powdered resin delivery from a flexible tube would be affixed and suction applied. The suction port would be under the agglomerate; this would prevent entry of powdered resin into the suction tube. Nevertheless, sufficient air channels are expected to exist to allow ready displacement of the air.

Figure 19 shows the free flowing nature of the powdered polyethylene employed in jacketing agglomerates. This material, flowing gravimetrically or pushed pneumatically, is expected to readily fill and intimately occupy an air evacuated cavity.

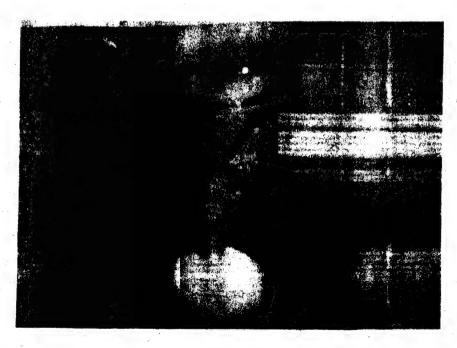


Figure 19. Powdered Polyethylene Seen Free Flowing Under Gravimetric Force

Figure 20 shows the five-sided resin jacketed agglomerate positioned for final resin jacketing. Powdered resin was applied and then fused onto the non-jacketed side.

Figure 21 shows the encapsulated hazardous waste emerging from the mold. Note the gap between encapsulated waste and mold walls. This was due to shrinkage of molten resin upon cooling, and it contributed to easy removal of the product.

Figure 22 shows a free-standing encapsulated waste.

Note the resin "flash" on the surface of the jacket about two-thirds down from the top of the product. Since only the non-jacketed side (as seen in Figure 20) was heated in the final jacketing step, some molten resin flowed into the gap between the relatively cool five-side jacketed agglomerate and the mold walls. During the final step, no appreciable heating of the resin jacket of the five side jacketed portion of the agglomerate occurred, and therefore it prevented expansion and possible distortion of the product. This advantage was due to the poor heat conducting property of the agglomerates. Were this fortuitous property not present, and agglomerates good thermal conductors, it would not be readily possible to localize sufficient thermal energy required for fusion of resin in the final jacketing step onto the agglomerate without product distortion. The resulting "flash", however, did not mitigate product performance.

Figure 23 shows a cross section of encapsulated hazardous waste. Figure 24 provides a close-up view of the cross section.

Inspection of the cross section and interface provided no visual evidence of seams in the resin jacket and showed intimate and tenacious adhesion of the resin jacket onto the agglomerate.

### 3.3.2 Additional Waste Passivation Study

The agglomeration and encapsulation method was applied to the arsenic containing waste described in Section 2.2 and to sodium chloride, the simulated waste material employed in prior work under Contract No. 68-03-0089.



Figure 20. Non-Jacketed Side of Agglomerate Seen Positioned for Final Resin Jacketing

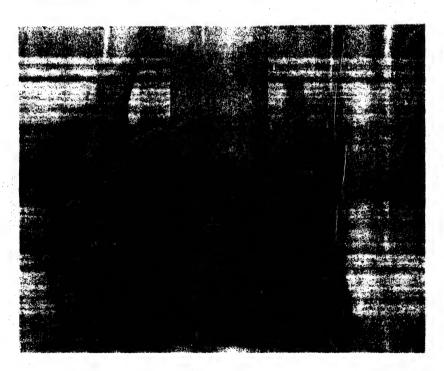


Figure 21. Encapsulated Hazardous Waste After Final Resin Jacketing Step

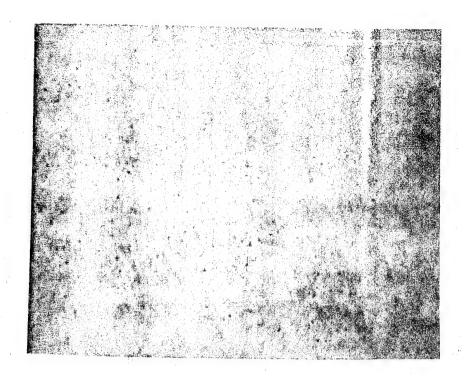


Figure 22. Encapsulated Agglomerate Seen After Final Resin Jacketing Step

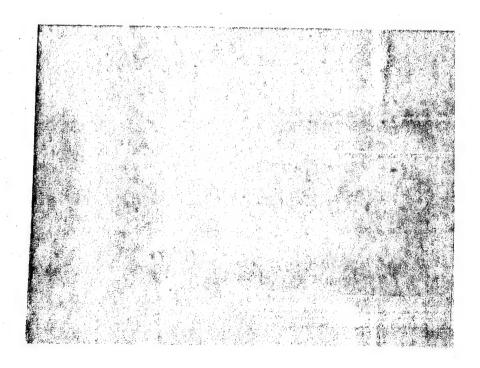


Figure 23. View of Cross Section of Encapsulated Hazardous Waste

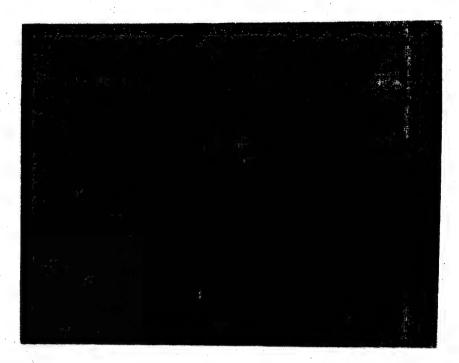


Figure 24. Close-up View of Cross Section of Encapsulated Hazardous Waste, a Blend Described in Section 2.2

The sodium chloride, as well as the arsenic containing waste, was used to evaluate the passivation method with respect to retaining contents of encapsulants characterized by highly water soluble salts.

With respect to both of the above materials, agglomeration and encapsulation were readily carried out. The nature of the passivated products is given in Figures 25, 26, and 27. Visual inspection of cross sections of encapsulated agglomerates of very water soluble materials provided no evidence of seams in the jacket. An interface area between agglomerate and jacket can be observed, this phenomenum resulting from partial penetration of jacketing resin into the agglomerate.

#### 3.4 SPECIMENS PREPARED FOR TESTING

Employing the method described above, 32, 3 inch cubical encapsulates, containing the waste blend described in Section 2.2, were prepared for the testing regimes of the following two sections. The encapsulates were characterized by 1/4 inch resin jackets encasing cube shaped agglomerates 2-1/2 inches on edge, with contents of 96% by weight heavy metal wastes. Of the same character, two encapsulates from the arsenic containing waste given in Section 2.2, and two encapsulates of sodium chloride were also prepared.

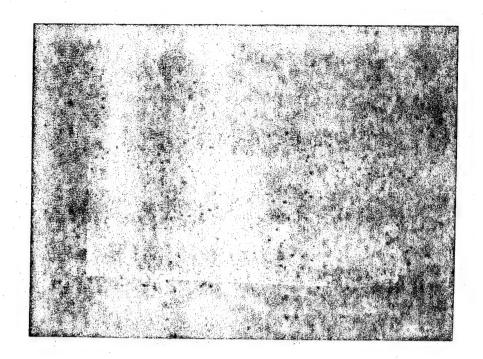


Figure 25. Cross View of Encapsulated Arsenic Containing Waste

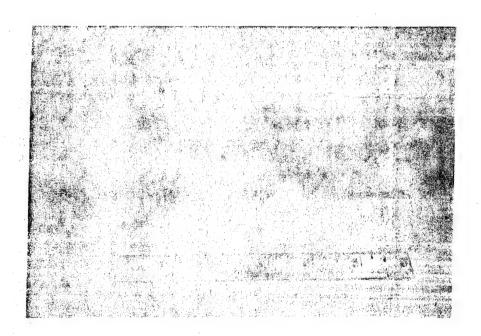


Figure 26. Polyethylene Jacketed Agglomerates of Sodium Chloride in Cross Section

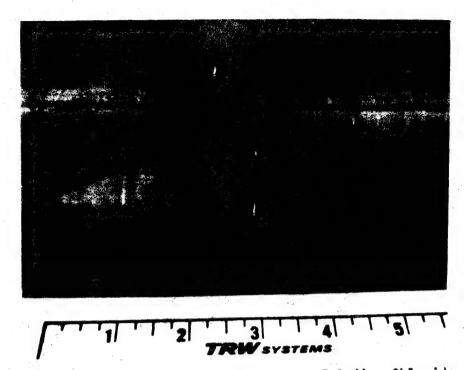


Figure 27. Polyethylene Jacketed Agglomerates of Sodium Chloride in Cross Section (Nearer View)

#### 4. LEACHING TESTS

The purpose of leaching tests was to demonstrate high performance capability of TRW encapsulated heavy metal wastes to withstand delocalization by ambient aqueous solutions stemming either from the ecological environment or industrial operations. Consequentially, a broad spectrum of aqueous solutions was employed for fashioning leaching baths, thereby encompassing solutions of exacting acidic and basic strengths, a simulant for ocean water, and one containing organic matter. Into these baths 3" x 3" x 3" blocks of encapsulated wastes, prepared as described in Section 3, were submerged and samples of bath solutions were withdrawn periodically for chemical analysis. This work, described in detail below, indicated that encapsulation provided high performance localization of heavy metals during leaching by exacting aqueous solutions.

#### 4.1 LEACHING PROCEDURE FOR COMPOSITE HEAVY METAL WASTES

The composite heavy metal waste described in Section 2.2, i.e., the combined residues of sludges designated by Vicksburg Experimental Station (Waterways sludges 200, 300, 500, 760, 800, and 900 from Table 1), were agglomerated and encapsulated. Sixteen blocks of encapsulated waste were employed. The blocks were placed in 2 liter beakers and submerged in duplicate in aqueous solutions. Figure 28 shows the encapsulated wastes under leaching conditions.

# 4.1.1 Trace Metals Assay Methods

The experimental procedure, analytical method, instrumentation and parameters used to determine the concentrations of the metal ions in the leaching baths are described as follows. The calibration graphs are given in Appendix B.

# 4.1.1.1 Technique

Environmental leaching studies were begun with the exposure of sixteen blocks to eight aqueous solutions: distilled water, 10% ammonium sulfide,

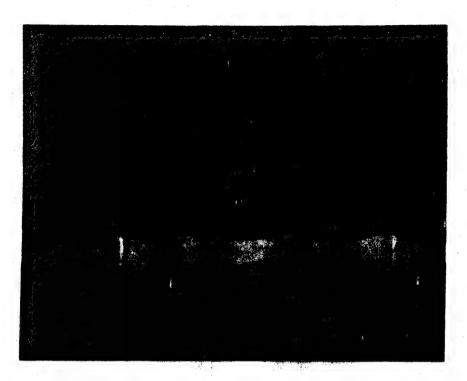


Figure 28. Close View of Encapsulated Wastes under Aqueous Solutions

1.5 N HCl, 0.1 N citric acid, 1.25 N NaOH, 0.1 N NH $_4$ OH, a simulated ocean solution, and 10% dioxane. All the leaching beakers, sampling glassware, and sample storage bottles were cleaned to prevent contamination from their use. They had a thorough wash with Alconox and were rinsed thoroughly with tap water. The glass beakers were washed with 3:1 HCl-HNO $_3$  (Aqua Regia), the glass volumetric flasks with concentrated  $\rm H_2SO_4$  warmed to 60°C and the plastic sample storage bottles with HClO $_3$  (20%) solution. The glassware was then rinsed thoroughly with distilled water. The sixteen blocks of encapsulated wastes were washed with distilled water and a brush to remove any surface contaminants.

Four liters of each solution were prepared using quantitative techniques. The initial pH and concentrations of the cations (Cu, Cr, Zn, Ni, Cd, Na, Ca and Hg) were determined for each solution. The blocks were then separated into two groups to provide duplicate determinations at alternate

data points. The encapsulated wastes were each immersed in 1200 ml of leaching solution. The solutions were sampled after 1, 2, 5, 10, 20, 30, 45, 60, 90 and 120 days. The remaining solutions were used to prepare calibration curves (see Appendix Figures B-l through B-8) and to maintain the volume of the leaching solutions to a level of total encapsulated waste immersion.

### 4.1.1.2 Testing Method

The Jarrell-Ash 810 Atomic Absorption Spectrophotometer was used for the determination of the concentration of all the cations with the exception of mercury. The mercury concentrations were determined using a LDC UV Monitor, Model 1205, and a stannous chloride reduction procedure.

At each time interval (1, 2, 5, 10, 20, 30, 45, 60, 90 and 120 days) 100 ml samples were drawn from the leaching beakers. The concentration effects involved with withdrawing samples were considered when calculating the concentration of the cations over the sampling period. When the volume of solution reached 700 ml, the blocks were still totally immersed; 100 ml of new solution was then added after each sample withdrawal, and the dilution effects were accounted in the concentration calculations.

The pH of the samples for atomic absorption analysis was adjusted to 2, wherever necessary, with nitric acid; the samples were analyzed using the parameters listed in Table 2. Four data points were determined for each element. Calibration curves, given in the Appendix, were established for each element in each solution.

The mercury content was determined by a cold vapor trap method. The mercury in the sample is reduced to the elemental state using a 10% stannous chloride solution and aerated from the system into the UV cell. The mercury vapor absorbs the UV (254 NM) according to its concentration in the fixed cell path. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner. The mercury calibration curves (Appendix, Figure A8) were established for all the solutions with the exception of the 10% ammonium sulfide. In order to liberate the mercury

TABLE 2. ATOMIC ABSORPTION PARAMETERS

Element	Slit (nm) Width	Analytical Wavelength (nm)	Background Wavelength (nm)	Gas Mixture	Detection Limit-ppm in Aqueous Medium	<u></u>
	1.0	324.7	323.4	Air acetylene	.003	1
	0.2	357.9	351.9	N,0 acetylene	.005	
_	1.0	213.9	210.0	Air acetylene	.003	
	0.2	323.0	231.6	Air acetylene	.01	
	0.4	228.8	226.5	Air acetylene	.003	
	0.4	589.0	3	Air acetylene	5.	
3	1.0	422.7	•	N <sub>2</sub> 0 acetylene	.005	
-	UV Monitor	254.0	•	1	.0003	

with this solution a special procedure would have to be established. Difficulty was also encountered with the simulated ocean solution and a pretreatment procedure was established. The procedure treats the solutions with the following oxidizing agents: 2 ml of 5% KMnO<sub>4</sub> and 2 ml of 5%  $\rm K_2S_2O_8$ . It was also necessary to use a 20% stannous chloride solution.

The sodium content was not determined in the NaOH,  $\rm NH_4OH$ , ocean and ammonium sulfide solutions. The calcium content was not determined in the ocean and ammonium sulfide solutions.

# 4.1.2 Compilation of Test Results

Tables 3 through 10 present heavy metal analytical determination of the selected leaching solutions in contact with duplicate samples of encapsulated waste over a period of 120 days. One set of determinations on each table shows heavy metal concentration of leaching solutions in contact with dry, untreated waste (unencapsulated waste). Although the concentrations of eight metals were sought, Cu, Cr, Zn, Ni, Cd, Na, Ca, Hg, some determinations were not possible due to interferences of substances in some of the leaching solutions.

# 4.1.3 Explanation of Leaching Tables

The tables give the mean cation concentrations in ppm and the standard deviation of the four readings that were conducted at each data point. These concentration values have been calculated from the calibration data generated for each leaching solution. The concentrations listed under the heading "Blank" give apparant values for the cations in the leaching solution before the immersion of the blocks. The values reported under "Unencapsulated Waste" are the cation concentration levels obtained by a 400 gram waste sample (approximately equal to the quantity of waste encapsulated) in 1200 ml of the particular leaching solution. The comparative data will clearly demonstrate the effectiveness of the encapsulation in preventing the solutions from solubilizing the waste materials. Table 11 reports the pH values of the solutions over the sampling time period.

TABLE 3. PPM CATION CONCENTRATIONS IN THE DISTILLED WATER LEACHING SOLUTION

	\$ 000+.001 0.035+.01 0.035+.01 0.05+.001 0.05+.002 0.05+.003 0.004 0.00+.003 0.00+.003 0.00+.003 0.00+.003 0.00+.003 0.00+.003 0.005 0.005 0.005 0.005 0.005 0.005 0.005 0.005 0.005 0.005 0.005 0.005 0.005 0.005 0.005 0.005 0.005 0.005	800.±500. 10.±6			600 -45200. 500 -45200. 500 -520 -500. 500 -520 -500. 500 -520 -500.				(Q)	COMMENTS ON LENGHING SOLUTION These encapsulated water concentration values a within the warletion of the background "instru- Same as above.  The sediam varietions are probably due to contain a sediam varietions are probably due to contain a sediam varietions are probably due to contain a sediam varieties are sediam varieties are sediam varieties. The sediam varieties are sediam varieties are sediam varieties and varieties are sediam varieties.
0. 0003+.0003	34.0003 .00034.0003 .00034.0003	.0004+.0003		.0004+.0003	.0007+.0003	.001+.0003	.0011+.0003	1200	X	0.005 ppm Percury was found in a baster of HCl free laboratory exposure only so it is difficult to
hese numbers he encapsular hese values a f unencapsula ng solution, ulated meteri	"Day" These numbers refer to the number of days the encapsulated waste has been immersel. "Unemerspalated waste on 120 ml of leaching sulated meters! is equal to the encapsulated meters!		lys is	Part per millio concentrations sample based on ratio. All values are "Unencapsulated	Part per million value of cation concentrations in the solid waste sample based on a Weight/Meight ratio.  All values are reported as parts.  "Unencapsalized Mastes" refer to	Part per million value of cation concentrations in the solid waste sample based on a Weight/Weight ratio. All values are reported as parts per million, PPH. "Unencapsulated Massas" refer to rea serve infa	Part per million value of cation concentrations in the solid wate sample based on a Weight/Weight ratio.  National and reported as parts per million, pen.			escribe the hy source.

PPM CATION CONCENTRATIONS IN THE SIMULATED OCEAN LEACHING SOLUTION TABLE 4.

COMMENTS ON LEACHTNG SONITTON	These energy within the	dental notse". Sepo as above.	Same as above.	Serre as above.	Some as above.	The Migher values in the second sample are probably due to surface contamination. They level off at these 20, surface contamination.	
DRY	MALYSIS (M/W) 76,923.0		770.0	153,847.0	384,616.0	154.0	
UNENCAPSU	91.40	0.34	1.50	0.40	983.5	1.05	
DAY	.003+.003	.0304.028	.007±.003	.004±.001	.042±.009	.0017±.0003	to dryIng
ξŠ	.003+.003	.030+.028	.007±.002	.055+.029	.042+.007	.0008+.0003	PPM. Ibjected only
DAY	.003+.003	820000	.011 <u>+</u> .004	.004+.001	200.±320.	.0016+.0003	Efe. Per million, raw westes si
YAC	.006+.006	.055±.028	.005±.004	.031+.026	.015+,001	.0011+.0003	Part per million value of catton Concentrations in the sold wash sample based on Neight/Neight-ratio. All values are reported as parts per million, PPM. "Unencapsulated Wastes" refer to raw wastes subjected only to drying
NAY 36	.040±.005	.022+.028	100.±100.	.037±.028	.016+.004	.001±.0003	per million v entrations in le based on He values are rep ncapsulated Ma
S S S	.008+.003	.0374.037	.002+.001	.0334.025	.017±.003	.0008+.0003	wlysis*
DAY 10	.007±.003	.0694,005	.015±.004	.086+.017	.0254,002	.002+.0003	TOTON T
DAY	.016±.003	.0514.003	.0024.001	.077±.045	.029±.003	.0011±.0003	These numbers refer to the number of days the encapsulated waste has been immersed. These values were determined for 400 greams for solution, which is mouel to the encapsulated maximum for solution, which is mouel to the encapsulated maxerial.
DAY	.003+.003	.058+.003	.007±.003	.107±.080	.020+.003	.001}+.0003	's refer to the lated waste has were determin lated weste on , which is map.
ķ-	.003+.003	.037±.037	.008 <u>4.</u> 005 .005±.003	020.±350.	.021±.004	.0007+.0003	These numbers refer to the nember of days "Unencapsulated maste has been immersed. "Unencapsulated These waldes were determined for 400 gress of unemcapsulated maste on 1200 ml of leach fog solution, which is wouse to the emcapsulated masterial.
BLANK	.003+.003	.030+,023	.016±.001	.004+.001	.033+.008	.0003+.0003	"Day" "Unencepsulate Kaste"
CATIONS	3	ბ	Ę.	¥	3	£	LEGENO

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PPM CATION CONCENTRATIONS IN THE NH40H LEACHING SOLUTION TABLE 5.

COMMENTS ON LEACHING SOLUTION	Incentration values are Dackground "Sestru-					ily due to surface appearant change from	*	
	These encapsulated waste concentration walues are within the veriation of the hackground "Kestru-mental nation".	Same as above.	Same as above.	Same as above.	Same as above.	These vertations are probably due to surface contamination. There is no experent change from Day 1 to Day 120.	Some leaching may be occurring	
AWLTSIS (WW)	76,923.0	163,847.0	770.0	153,847.0	384,616.0	153,847.0	154.0	
UNENCAPSU-	414.0	710.9	17.4	1.0	0.86	23.0	9.26	
DAY BE	310300.	500°-1000°	.001±.00	.088±.044	.010084	. 615+, e03	.0013+.0003	
AYC AYC	100.480	.003+.001	.001±.001	.091±.066	.017+.004	.018+.009 .060+.028	.0015+.0003	
DAY 66	.008+.006	1900000	.001±.001	.065±.046	. 663+, 902	180 -180	0008+-0083	
PAY 25	900.±900.	.005±.005	.006+.003	.024+.013	.013±.004 .009±.003	.044+.007	.0006+.0003	ion of cation
BAY 8	900900	900-+600	100.±100.	\$20.±0%.	100 TO20	200 200	.0011±.003	Part per million of cation
DAY 28	.013±,003	.096±.004	.001±.003	.0164.016	.006±.003	.047±.005	.0007+,0003	"Dry Analysts"
DAY 10	.006+.003	100° <del>-</del> 1600°	¥00.+500°	.025±.011	.007±.003	.024+,003	£000°∓¥000°	
DAY 5	.005+.003	640.±360.	£00.±100.	.069:.037	.013±.006	.066±.080	.0004 <u>+</u> .0003	number of de
DAY	.005±.005	.005±.005	100.±100.	.0524.022	.012±.006	100.4350.	.0004+,0003	These numbers refer to the number of days
DAY 1	.003+.003	.006±.006	900°∓900° 200°∓900°	.024±.007	.001±.001	\$60.±350.	.0003+.0003	These number
BLANK	.008+.004	.003+.003	100.+100.	.024±.007	.001±.001	.003±.004	.0003+.0003	"Day"
CATIONS	3	ბ	r,	E	8	8	2	LICEND

All values are reported as parts per million, PPM. "Uncapsulated Mastes" refer to rew wastes subdected only to drying

NOTES:

PPM CATION CONCENTRATIONS IN THE NAOH LEACHING SOLUTION TABLE 6.

COMMENTS ON LEACHING SOLUTION	These encapsulated waste concentration values are within the variation of the background "instrumental noise".	Same as above.	These values are probably due to surface contamination. There is no apparent change from Day i to Day 120.	Same as above.	These encapsulated waste concentration values are within the variation of the background "instrumental noise".	Same as above.	Samu as above.
Š	76,423.0	153,847.0	770.0	153,847.0	384,616.0	153,847.0	154.0
UNENCAPSIL	139.1	5,884.5	15,519.8	not detected	1,500.3	44.3	0.005
DAY	120 	.003±.001	.021±.001	.068±.042	.016+.005	900-+900-	.0003±.0003
PAY	.017±.003 .003±.008	.014±.009	.019±.003	.073+.060	200°+900°	.00 <u>6+</u> 0.0	.0003±.0003
DAY	.040±.012	.010+.004	100.4840.	.067±.026	.012±.003	0.04-900.	.0003+.0003
DAY	.040±.040	.003+.003	.013±.003	.119±.035	.002±.001	.020+.003	.0003±.0003
DAY	.034+.034	.0934.093	.0154.003	900-∓900°	700°+500°	.030+.002	.0003+.0003
DAY	20 .019±.001 .031+.010	.010+.005	.035±.004	.008±.008	.007±.002	.004±.001	.0003+.0003
DAY	10.0244.005	.003±.004	.052+.007	.0194,013	£00.±010.	.011 <u>+</u> .002	.0003±.0003
DAY	.012±.005 .021±.005	.005±.005	.026±.001	.032±.012 .076½.040	.004+.003	.037±.003	.0003+.0003
DAY	.013+.003	500.± <u>₹</u> 500.	.121 <u>+</u> .005	.012±.012	¥00. <u>±</u> 110.	.068±.003	.0003+.0003
ρĀ	.008+,004 .006+,005	.0144.605	.118±.004 .104±.004	.019±.013	.005±.006	.062+.005	.0003+.0003
BLANK	.0034.004	.0034.004	.003+.003	.019 <u>~</u> .013	.018±.007	.007±.007	.0003+.0003
CATIONS	ē	ర	Ę	Ξ	8	3	£

LEGENO

These numbers refer to the number of days the encepsulated waste has been immersed. "Unancapsulated These values were determined for 400 grams Maste" of unexcipsulated maste on 1200 M. of leaching solution, which is equal to the encapsulated material.

"Ory Analysis" Part per million of cation
concentrations in the solid waste
sample based on a Neight/keight
ratio.
MOTES: All values are reported as parts per million, PPM.
"Umencapsulated Mastes" refer to raw wastes subjected only to drying

PPM CATION CONCENTRATIONS IN THE AMMONIUM SULFIDE LEACHING SOLUTION TABLE 7.

		7			1	_
CONTENTS ON LEACHING SOLUTION	These encapsulated waste concentration values are within the variation of the background 'instrumental noise".	Same as above.	Same as above.	Some as above.	Same as above.	
	76,923.0	153,847.0	770.0	153,847.0	154.0	
UNENCASIL LATED WASTE	2.9	233.4	90.0	2388.9	8.3	
DAY 120	.061±.002	.009+.009	.114+.002	.093+.043	. CB6+. OG3	
ğ R	.006+.002	600.±800.	121001	.177±.028	.084+.003	
ş	.018+.002	600 · +600 ·	.083+.002	.249±.030	.094+,003	
şş	200.+200	600.±600.	.003±.002	.060+.050	.091±.003	on of cation
žπ	.010+.002	600°+600°	.063 <u>+</u> .004	520.±5.00.	900.4900	Part per ad]]i
Ŕ	.002+.002	600.±600.	.004.001	.110 <u>+</u> .017	.012 <u>+</u> .075	"Dry Amalysis" Part per million of cation
32	200°∓200°	.004+.002	.028+.002	.034+.025	.0954.003	
35	2007+2007	.000±.000 .000±.000	.163±.004	.073+.040	.142±.006	These numbers refer to the number of days
<u> </u>	100. 100. 100. 100. 100. 100. 100. 10	.004±.002	.031±.004	.094+.051	.0574.006	ers refer to
<b>i</b> -	200.+810.	.003+.006 .009+.009	.050±.003	.119±.064 .030±.030	.063+.006	These num
NA.	.018+.002	600.±900.	.006±.006	.030±.030	.073+.010	À
200	8	8	A	E	3	00001
	1 2 5 10 20 30 45 60 70 130 LATED WASTER AMALTSTS (WAL		### 1819   1914	-818±-002	- 119±-002	- 618±-002

NOTES: "Unemclapsulated These wiless were detarmined for 400 grass feate"
for solution, which is equal to the encapsulated material.

All values are reported as parts per million, PPM. "Unencapsulated Mastes" refer to raw wastes subjected only to drying

PPM CATION CONCENTRATIONS IN THE CITRIC ACID LEACHING SOLUTION TABLE 8.

Γ	۽ ۾		are '			Mange	or to	are	7
COMMENTS ON LEACHING SOLUTION	There is no in one set o	Same as above.	These encapsulated waste concentration values are within the variation of the background "instru-mental poise".	Same as above.	Same as above.	These concentration values are probably due to surface contamination. There is no apparent change	rrom Lay 120.  An increasing trend is noted. This could be due to surface contamination because a similar trend for Ma	(above) which would be expected also is not observe. These encapsulated waste concentration values are within the variation of the background "instrumental noises."	
DKY	76,923.0	153,847.0	770.0	153,847.0	384,616.0	76,923.0	153,847.0	154.0	
UNENCAPSU-	1,803.4	2,528.7	18,270.3	4,719.3	6,401.3	6,085.0	21,537.6	.004	
PAY	.010+.005	.012+.034	.008±.003	.055+.055	.0524,004	.035+.001	.345±.014	.0005±.0003	to drying
AY DAY	.010+.005	.013+.094	.003+.003	.194+.050	900.±860. .086±.004	.0145.001	.290±.015		Part per million of cation concantrations in the solid wate sample based on a Weight/Neight ratio. All values are resorted as parts per million, PPM.
¥5	.010+.006	.014+,005	.003+,003	,015+,015	200.+650.	.006+.001	.274+.002	.0004+.0003	aste ht rts per millio to raw waste
PAY	.041+.054	.0304.005	.001+.0005	.031 <u>+</u> .019	.042±.004	.078+.003	.129+.003	.0004+.0003	n of cation in the solid w a Weight/Neig reported as pa Wastes" refer
AV.	.019±.00	.0034.005	.001±.001	.024+.014	.044.004	.094+.003	.207±.008	.0011±.0003	Part per million of cation concentrations in the solid wate sample based on a Weight/Neight ratio. All values are resorted as parts per million, PPM. "Unencapsulated Wastes" refer to raw Wastes subjec
¥g	.009+.008	.005±.003	.005±.002	.030+.030	.044±.003	.054+.001	.541+.013	.008+.0003	"Dry Analysis" Pr
DAY 10	.010+.007	.011±.000	.005+.001	.076+.020	.048+.003	100.±060.	.063±,006	.0006+,0003	
DAY	.013+.004	.004+.004	.006±.005	.054±,031	.123±.007	.224+.002	.502+.020	.0007±.0003	the number of cas been immers ined for 400 gon 1200 ml of qual to the en
DAY	. 005+, 005	.002*.002	100.±500.	.0724.047	.031±.002	.076+.001	.041+.006	.0003+.0003	These numbers refer to the number of days the encapsulated waste has been inmersed. These values were determined for 400 grams of unercapsulated waste on 1200 ml of leach-sulated material
DAY	.003+.004	.003+.004	.002+.001	.037±.037	.090±.002	.255±.006	.360+.005	.0003+,0003	
BLANK	.003±.003	.003+.003	.001±.001	.037±.037	.000 <u>6+</u> .0006	.001±.0005	.010±.010 .010±.010	.0003+.0003	"Day" "Umencapsulated Waste"
CATIONS	з	5	<b>4</b> 2	E	3	£	3	£	ONE SECTION

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TABLE 9. PPM CATION CONCENTRATIONS IN THE HC1 LEACHING SOLUTION

UTION	probably due to	stration values are Aground "instan-				probably due to freg.	probably due to s no apparent	however, at 90 days a beater of HCI from a different to
COMMENTS ON LEACHING SOLUTION	These	These encapsulated waste concentration values are within the waitation of the background "instan-	Same as above.	Some as above.	Same as above.	These concentration values are probably due to surface contamination and handing.	These concentration wiles are probably due to starfor containstition. There is no apparent channe from Inv. 1 to Eu. 150.	Some leaching may be eccurring, however, at 90 days 8,0015 pan Mercury was found in a beatur of Hillboar laboratory economic many se it is 44444-111
AMAI VETE (14.02)	76,923.0	153,647.0	770.0	153,847.0	384,616.0	76,823.0	163,847.0	154.0
UNENCAPSUL LATED WASTE	25,035.0	127,380.0	8,231.7	42,382.0	106,416.0	45,008.5	690,660.0	171.5
9AY 120	.011±.004	10.4369.	.011±.005	.168±.074	200.±610.	.218+.004		.0189+.0003
DAY 8	.028+.004 .020+.003	.071+.012	.008+.003	.107+.056	.070+.006	.1664.602 .1244.002	.015±.006	.0149+.0003
DAY 86	700.±110.	300060-	100. 100.	.039+.022	.015+.003	.1612.083		.0136+.0000
DAY 45	.007+.004	.042+.017	.004002	.017±.017	.108+.003	.360+.013 .070+.002		.014+.0003
DAY 30	010.±510.	.111 <u>1</u> .025	. B83±. 002	.014±.007	.020+.002	.052+.007	.062+.009	.013+.0003
DAY 28	.0034.005	.112±.089	.002+.002	.048+.030	.0254.002	1.03+.002	.317±.020	.016+.0003
P¥ 0	100.±100.	600.4710.	.016±.006	.101+.080	.029+.003	167+.001	.121+.070	.01840003
DAY 5	.002+.003	.100±.009	.010±.002 .022±.003	.015 <u>+</u> .015	.117±.007	1334.001	.363+,020	.010±.0003
DAY 2	900.+600	.007±.010	100°+300°	.075±.033	900 -910	.300003	. 567±, 620	.002+, 8003
<b>₹</b> -	.010+.00	.017±,006	.024+.004	090-7-690	700020.	200.+821.	.097+.097	.0012±.0003
BLANK	.0025+.0038	.0364.01	.008+.006	.065±.023	200.±e00.	200.+100.	.003±.003	.0000000
CATIONS	3	<b>5</b>	ā	ä	2		3	£

"Unencapsulated Maste" LEGENO

These numbers refer to the number of days
the encapsulated waste has been immersed.

These values were determined for 400 grams
of amencapsulated waste on 1200 ml of leachfing solution, which is equal to the encapsulated material.

All values are reported as parts per million, PPM. "Umencepsulated Mestes" refer to raw wastes subjected only to drying

PPM CATION CONCENTRATIONS IN THE 10% DIOXANE LEACHING SOLUTION TABLE 10.

	COMMENTS ON LEACHING SOLUTION These encoulanted wash	within the variation of the background "instru- mental noise".					e is increasing. In Within the variation	tmental noise".	res are probably due to There is no apparent	120			inese encapsulated waste contemination values are within the variation of the background "instru- mental noise".		
	These encapsulated maste control	within the variation or mental noise".	Same as above.	Same as above.	Same as above.		The cadmium in one sample is increasing. In the other the walues are within the variation	or the Deckground Thatr	These concentration values are probably due to surface contamination. There is no apparent	change from Day 1 to Day	Same as above.		inese encapsulated waste contamination values ar within the variation of the background "instru-		
Ago	3	76,923.0	153,847.0	770.0	153 847 0		384,616.0		76,923.0		153,847.0		154.0		
UNENCAPSIL	LATED WASTE	5.9	71.6	1.6	5.5		19.5		4834.3		134.9		0.002		
DAY	120		.004+.004	.004+.001	.002+.001		.037±.005		.610+.006		.146+.010	0003+ 0003	5000		
DAY	.0414.013	.008+.005	.003+.004	.008+.001	.002+.001	'	.015+.004		.258+.003		.015+.001	-			sample based on a Weight/Meight Tatio. Tatio
DAY	.012+.008	200		.010+.001	.002+.001		.034+.005		.392+.006	TOW THOU	The state of the s	.0003+.0003	1	aste	ht ints per silli
DAY	.008+.004	-003+-003	.002+.003	.007±.004	.002±.001		.024+.003	200.	.2914.002	0 1034 DOG	.0762.005	.0007+.0003	.0004+.0003	n of cation in the solid w	a Weight/Weig reported as pa Wastes" refer
Ş. P.	.008+.004	-005+.005	1	.007±.004	.002±.001		900.4520.	3001 000		.094+.005	1	.0003+.0003		Part per million of cation concentrations in the solid waste	sample based on a Meight/Meight ratio. All values are reported as parts per million, PPM. "Unencapsulated Mastes" refer to raw waters envises.
DAY %	.005+.005	.0054.001	.007+.001	.0034.003	.0024.001	1010 TO10	.005±.004	350+ 005	.145+.001	.008+.007	0.1704.002	.0003+.0003	.0003+.0003	"Ory Analysis" P	NOTES: A
DAY 10	.002+.002	100.+100.		.00€±.003	.002±.001	10034 001		.426+.005	1	.008+.007	ı	.0003+.0003			
DAY 5	.011±.003	.005+.003	100.4800.	.023+.004	.002±.001	.004+.002	.004+.004	.548+.004	.1694.003	.012+.001	.200003	.0003+.0003	.0003+.0003	e number of designations	ned for 400 gr n 1200 ml of j sal to the enc
DAY 2	.005±.005	.006+,003		.009+.002	.002+.001	.000+·004	ı	.941+.012		.030+.007		.0003+.0003		These numbers refer to the number of days the encapsulated waste has been immersed.	These values were determined for 400 grams of unencapsulated waste on 1200 ml of leach- ing solution, which is equal to the encap- sulated meterial.
DAY 1	.003+.004	.008+.001	.004±.004	.014±.007	0.0024.001	.006+.004	.011+.007	1.0194.010	.172+.002	.029+.008	.130+.003	.0003*.0003			
SLANK	.008+.004	.016+.016	910410.	.007±.004	0.0+0.0	.003+.003	.003+.003	.004+.0085	.004+.0035	.008±.094	.008+.004	.0003+.0003		"Day"	"Unencapsulated Naste"
CATIONS	3	ర		<b>4</b> 3	£	3	,	2		3		호		LEGEND	

48

TABLE 11. PH VALUES OF LEACHING SOLUTIONS

Solution	0 Day	1st Day	2nd Day	5th Day	10th Day	20th Day	30th Day	45th Day	60th Day	90th Day	120th Day
Distilled Water	6.3	6.8 7.0	7.0	6.00 8.70	6.5	6.6	6.2	8.5	7.0	5.7	6.1
HCT.	0.3	0.4 0.5	0.6	0.7	1.1	0.3	0.5	0.0	0.8	0.9	0.8
Citric	2.2	2.5	2.5	2.8 2.8	2.3	1.9	2.1	1.8	1.6	1.6	1.7
NaOH	11.5	12.1 12.1	12.1	11.8 12.0	11.8	12.9	12.5	12.9	13.0	12.9	13.0
MH <sub>4</sub> OH	11.1	4.0	9.4	8.8 9.9	8.8	8.6 8.6	9.0	<b>8</b> 8 8 8 8 8	8.6	9.2	8.2
Ocean	6.1	6.5	6.3	8.4	8.2	9.4 9.6	9.5	9.3	7.7	7.5	7.7
Dioxane	4.8 5.3	4.6 5.1	5.0	6.7	6.2	6.0	4.5	<b>4.7</b> 5.7	4.7	3.8	4.2
Ammonium Sulfide	8.8	8.7	8.6	8.7 8.7	8.7	7.2	9.1	8.8	9.0	9.4	9.5

#### 4.2 LEACHING PROCEDURE FOR ARSENIC CONTAINING WASTE

The arsenic waste described in Section 2.1, i.e., the waste containing 1-1/2% by weight monosodium methylarsonate, 49% sodium chloride and 49% sodium sulfate, was agglomerated and encapsulated. Two blocks were utilized in the leaching studies. The blocks were placed in 2 liter beakers, one submerged in distilled water and the other in a 1.5 N HCl leaching solution. Table 12 gives data concerning arsenic and sodium concentrations of the leaching baths over 80 days.

### 4.2.1 Arsenic Assay Method

The experimental procedure and the analytical method used to determine the concentration of the arsenic in the leaching baths is described below. The sodium content was also determined in these solutions by atomic absorption spectroscopy using the parameters given in Table 2.

#### 4.2.1.1 Technique

The glassware, blocks and solutions were prepared according to the procedures used for the composite heavy metals waste samples. The leaching of arsenic containing blocks were conducted over a period of 80 days with samples being analyzed for their arsenic content at 1, 2, 5, 10, 20, 30, 45, 60 and 80 day intervals. A sample of the dry, untreated waste material was also placed in the water and acid solutions and analyzed for its arsenic content after 80 days of exposure to provide a comparative data point for establishing the effectiveness of the encapsulation in containing this hazardous material.

# 4.2.1.2 Method of Analysis

Inorganic arsenic is reduced to arsine, AsH<sub>3</sub>, by zinc in acid solution. The arsenic is then passed through a scrubber containing glass wool impregnated with lead acetate solution and into an absorber tube containing silver diethyldithiocarbamate dissolved in pyridine. In the absorber, arsenic reacts with the silver salt, forming a soluble red complex which is suitable for photometric measurement. The absorption is then measured

PPM ARSENIC AND SODIUM CONCENTRATIONS IN DISTILLED WATER AND HC1 LEACHING SOLUTIONS

Solution	Blank	Day 1	Day 2	Sec.	Day 10	2 S	30 kg	Day 45	33	90 N	Unencapsu- lated waste	e Comments
Distilled Water	10.>	.0.	10.^	10.^	٠.01	٠.01	0	.0.	۰.0j	<b>10.</b> >	2,420	No arsenic was detected in this leaching solution.
Arsenic 1.5 N HC1	.00	.01	<b>6.</b> °	. <b>2</b> .	.00	·.01	·.01	·.0.	·.0	<b>.</b> .0	1,017	Same as above
Distilled Mater	.050+.002	.050±.002 .191±.006 .129±.003	.1294.003	.148+.002	.189±.001	.1784.001	All an	All available solution was used in arsenic	Jutton	.21±0	10,085.4	10,085.4 Mo sodium was detected. Day 10,085.4 Mo sodium was detected. The within the variation of the
Sodium 1.5 N HCl	.002±.001	.164±.001	.076+.062	.069+.003	.069+.003 .069+.002 .150+.002	.150+.002	A S S S S S S S S S S S S S S S S S S S	determination. All available solution was used in arsenic determination.	olution	.176+.002	10,918.9	"instrumental noise". 10,918.9 Same as above

<u>LEGEND</u>: Days - These numbers refer to the number of days the encapsulated waste has been immersed. Unencapsulated Maste - These values were determined for 400 grams of unencapsulated waste on 1200 ml of leaching solution, which is equal to the encapsulated material.

Values are reported as parts per million, ppm.
Arsenic was determined by the silver diethyldithiocarbamate method.
Sodium was determined by atomic absorption spectroscopy.

on a spectrophotometer at 535 millicrometers. A Beckman DK-2 spectrophotometer was used for these determinations and was calibrated using standards of 0.2, 0.4, and 0.6 ppm. The limit of detection for arsenic using this method is 0.01 ppm. Duplicate determinations were conducted for each analytical run.

### 4.2.2 Explanation of Table

The data reported in Table 12 for the arsenic levels in a sample of unencapsulated waste material are equal to the concentrations that would be obtained for 400 grams of waste in 1200 ml of solution after 80 days, which is approximately equal to the weight of waste contained in each sample block. If a zero absorption reading was obtained, the concentration value was reported as less than 0.01 ppm limit of detection. Due to the nature of this waste the solutions were also analyzed for their sodium content by atomic absorption spectroscopy.

#### 4.3 ASSAY OF ENCAPSULATED SODIUM CHLORIDE

Two encapsulated blocks of sedium chloride weighing 538.6 g and 536.8 g were submerged in water over a period of six months. The blocks were periodically removed and weighed. No weight change of the blocks could be observed which exceeded the sensitivity of the determinations, i.e.,  $\pm$  0.1 g.

#### 4.4 DISCUSSION OF LEACHING TESTS

No definite trend of increasing concentrations of any of the monitored metals was noted in any of the leaching baths Tables 3 to 10. Mercury may be an exception in two cases: HCl and NH<sub>4</sub>OH solutions. However, laboratory contamination may account for this increase since 0.0015 ppm mercury was observed in a blank sample of the HCl leaching solution after 90 days of exposure in the work area. Analogous sample contamination have been observed by others.\*

Bothner, M. H. and Robertson D. E.; Analytical Chemistry, Vol. 47, No. 3, March 1975, page 592.

The erratic values observed for the concentrations of any one metal from one time period to the next are due to the low concentrations present. This results from analyzing for metal ions at the limits of detection and, therefore, includes the instrumental noise.

Calcium and sodium in trace amounts appear to be surface contaminants of tested specimens. Since sodium is present in hand oils and both calcium and sodium are present in tap water, slight traces of sodium and calcium could be left as residues on all washed surfaces. Trapped particulates on the surface may account for some concentration readings, i.e., cadmium in the distilled water solution, where the ion value after the first day of immersion is the same as after 120 days.

Of particular importance, Tables 3 to 10 show that the concentration of any given metal in the encapsulated waste is low and equivalent in all the leaching baths after 120 days of immersion. Yet the concentration values of the metals of unencapsulated waste are usually high and vary widely with the nature of the bath employed. Particularly noteworthy are the results given in Tables 8 and 9. These show that excellent retention of heavy metal contaminants was realized even in the presence of strong solvents such as citric acid and HCl. Table 11 shows that the pH of the solution did not vary during the leaching period, the slight changes in the values given being attributed to the margin of error of the determination. And Table 12 shows that retention of arsenic and sodium was excellent. Such data indicate that essentially equal effectiveness is maintained by the resin jacket in retaining a wide range of heavy metal contaminants under a broad range of leaching conditions.

# 5. MECHANICAL TESTS

Mechanical testing was performed on the encapsulated blocks of hazardous waste materials to determine their behavior during handling, transportation, storage and disposal, as well as subsequent environmental exposure. A test plan was made to evaluate the mechanical properties of the encapsulated waste (Table 13). Thirteen specimens of a blend of mixed wastes were employed (composition and fabrication method given in Section 2.2 and Section 3.3, respectively) and subjected to the mechanical testing.

# 5.1 COMPRESSION

The compression test indicates the ability of the specimens to with—stand loads at the disposal sites. The test is based on ASTM-C-39-71, but was modified to use cubic specimens. The ultimate compressive stress of the specimens was defined as the maximum load in the load-deformation curve (Reihle testing maching) or the maximum indicated load using the Cal-Tester testing machine, divided by the cross-sectional area of the specimen.

# 5.2 FREEZE-THAW TESTING

The test was employed to determine the ability of the jacketed blocks to withstand thermal cycling in a landfill environment. The test is a modification of ASTM-C666-71 and consists of thermal cycling of the jacketed blocks alternately in a -10°C salt/ice bath and 100°C boiling water. The cycles were of 15-minute duration (16 full cycles per day) with the blocks being stored in a freezer during overnight periods. The tests were continued for 75 half-cycle temperature changes and then they were tested for ultimate compression strength as discussed in the preceding section.

TABLE 13. MECHANICAL TESTING PROGRAM FOR HAZARDOUS WASTE ENCAPSULATION PROGRAM

#	Test	Number of Specimens Employed
1	Compression	3
2	Freeze-Thaw	3
3	Impact Strength	3
4	Puncturability	
5.	Bulk Density	3

## 5.3 IMPACT STRENGTH

This test indicates the ability of jacketed blocks to withstand mechanical impact as may occur during transportation or dumping of the blocks. While a standard dart type impact test such as the Izod or Gardner tests would be desirable for comparison with other materials, these tests require a specimen of specific geometry using a flat .060" to .125" thickness specimen. Therefore, a drop test was utilized for the cubic specimens which was a minor modification of ASTM D997-50-71, Impact Strength of Cylindrical Shipping Containers. The specimens were dropped onto a steel plate 50 times from a height of 6 feet, followed by 15 drops from 10 feet and 30 feet.

### 5.4 PUNCTURABILITY

This test was designed to measure the resistance of the jacketing material to puncture by sharp objects. Initially, Federal Test Method 101B, Puncture Resistance, was chosen as the test method, but the configuration of the specimens and jacket thickness precluded the use of this method to obtain satisfactory data. A qualitative test was then employed in which a pointed tip steel fixture was made for use with the compression fixture in the

Cal-Tester testing machine. Figure 29 gives the dimensions of this test fixture. This test is qualitative, but will indicate the general mode of failure of the tested specimens as well as penetration force. Data were obtained for the jacketed specimens in the testing. A loading rate of .050"/minute was used.

## 5.5 BULK DENSITY

Bulk density measurements were performed on inner core blocks of the mixed hazardous waste. This was accomplished by carefully weighing and measuring three blocks and determining an average bulk density and the deviation from the average for the individual specimens.

# 5.6 RESULTS OF MECHANICAL TESTING

The results obtained in mechanical testing are provided as follows:

Compressive Strength of Virgin Products
Compressive Strength after Freeze-Thaw
Impact Strength
Puncturability
7
Bulk Density of Agglomerate

1523 psi (87)<sup>(1)</sup>
1335 psi (228)<sup>(2)</sup>
withstands 30 ft drop<sup>(3)</sup>
700 pounds<sup>(4)</sup>
92 lb/ft<sup>3</sup> (.14)<sup>(5)</sup>

- (1) Standard deviations given in parenthesis. Figure 30 shows a typical loading deflection curve in compression of encapsulated products.
- (2) The property determination and observation of specimens indicated that the encapsulated products are stable in freeze-thaw.
- (3) Figure 31 shows a specimen after cumulative 6 foot, 10 foot, and 30 foot drop exposures.

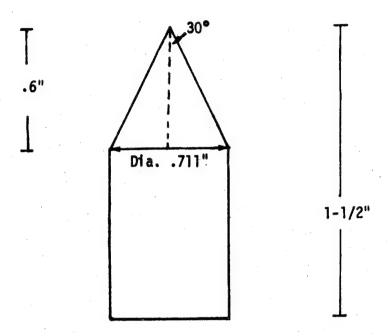


Figure 29. Jig Used For Puncturability Testing

- (4) It required a 700 pound force to penetrate the 1/4 inch jacket to the surface of the encapsulated agglomerate. No fracture on crazing occurred in the vicinity of the puncture.
- (5) Observation of the surfaces of the agglomerates showed homogeneous distribution of the particulates.

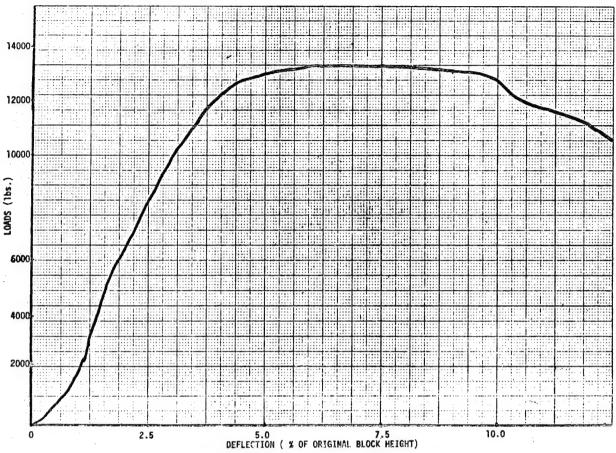


Figure 30. Load-Deflection Curve for Compression Testing of Jacketed Block Specimen

# 5.7 DISCUSSION OF RESULTS

Within the constraints of the program only preliminary mechanical evaluations could be carried out. The limited number of tests and specimens employed does not provide at this point sufficient information to completely characterize the mechanical performance response of encapsulated wastes under real life conditions. However, the results do indicate that high mechanical performance will be achieved.

The magnitude of the compressive strengths showed encapsulated products to be equivalent in strength to Portland cement. They should be capable of sustaining the unidirectional pressure of 1500 psi (equivalent to a 3000 foot column of water).

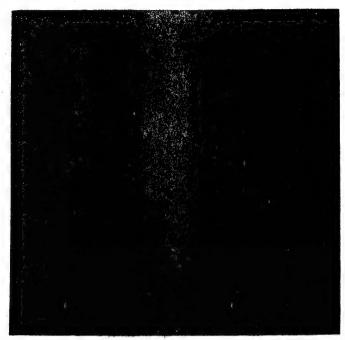


Figure 31. Jacketed Specimen After Impact Testing

Excellent product integrity is expected under actual freeze-thaw conditions. The temperature range employed in this study was greater than that likely to be encountered in a landfill, yet the products maintained functional integrity. Furthermore, the products withstood the additional stress of thermal shock. This stress although not present in a landfill may be encountered in product fabrication, handling and transportation.

In the impact test, the products were dropped from appreciable heights. With the exception of deformation of the edges, the products sustained the stress of impact without apparent damage. Under use conditions, the products after being dropped from the bed of a truck either in transport or in charging a landfill should continue to maintain functional integrity.

The requirement of 700 pounds pressure from a directed, pointed metal jig to penetrate the jacket of the products showed that the products are characterized by outstanding ability to withstand puncture. Even with penetration, no cracking, crazing, or indeed any other indication of

failure occurred in the vicinity of puncture. The product jacket under stress of puncture alleviates the stress plasticly, thus conserving the hazardous consignment. Only with complete penetration of the jacket will the contaminants be exposed to the environment. And even then, the amount of exposure will be limited to the area formed in pertrusion by the puncturing object. No spillage will occur because the contaminants are confined in a matrix.

The density of the products are in the lower range of the density characterizing the earth, i.e., 90 to 200  $lbs/ft^3$ . Ground phosphate rock through 8 mesh exhibits about 100  $lbs/ft^3$  bulk density.

Observation of the specimens after testing gave rise to the conclusion that future specimens must be fabricated without sharp edges. All of the evident damage to the specimens in testing was seen on the edge of the samples, see Figure 31. The cubic and rectangular shapes are desirable because they contribute to efficient use of space desired in transporting and perhaps even in final disposal of the encapsulated wastes. As a result, it is desirable to retain these configurations as much as possible. But future specimens must be characterized by rounded rather than sharp edges. The determination of the optimum shape of an encapsulated waste product should be addressed in future work.

# 6. DEVELOPMENT OF THE GENERAL PROCESS AND PROCESS ECONOMICS MODEL

Concurrent with work relative to determining the technical character of the TRW process and to demonstrating the performance properties of its products, additional work was directed to defining the nature of a large scale process and to assessing its associated costs. In this work element, a mechanical means was set forth for fabrication of large-sized passivated waste products; and the dimensional nature of cost effective products was estimated. Attendant equipment required for plant operations, and a plant operational procedure were summarized in a Process Flow Diagram. Based upon the structured process, a computer model was provided and it was employed to perform economic evaluations. From these evaluations, the cost was determined for producing products; cost sensitive areas were identified for additional investigation in order to further reduce costs.

# 6.1 PROCESS DEVELOPMENT

In the development of the engineering process, a mechanical means and technique suitable for large scale passivation operations was set-forth to carry out agglomeration and resin jacketing of hazardous wastes. A metallic sleeve that is detachable from a stepped platform (Figure 32) forms a mold for agglomerating resin coated particulated waste. Thermal energy is transmitted to the waste while moderate mechanical pressure is applied. The waste is immobilized by the thermosetting reaction of the resin and a free standing agglomerate is thus obtained upon withdrawing the sleeve. A second sleeve of larger dimensions is lowered about the agglomerate followed by evacuation of the air from the annulus formed between sleeve and agglomerate. Powdered polyethylene is then sucked into the annulus. Suction would be applied through a port beneath the agglomerate. Heat is applied through the sleeve to melt the plastic and, after cooling, a five-side jacketed agglomerate is produced. The agglomerate is then righted for final jacketing. A seamless seal between the "bottom" and "side" jacket is effected because the "lips" of the "side" jacket are remelted during the final jacketing operation. The agglomerate is thus thoroughly encapsulated by a continuous resin jacket.

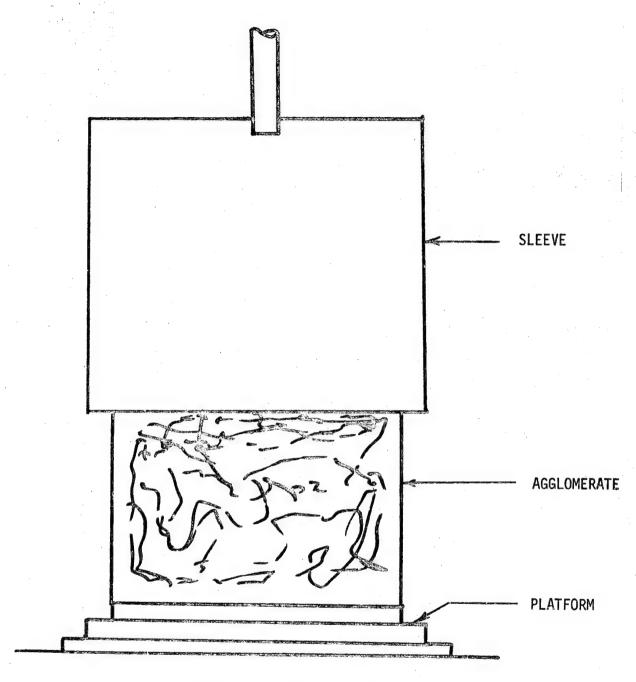


Figure 32. Process Concept

This agglomeration and encapsulation technique does not require molten resin to be employed outside the mold. Metallic tubes, screw conveyors, and mechanical rams required for molten resin delivery systems are not necessary. Flexible rubber hoses can be readily employed for delivery of powdered resin at room temperature to the mold. As a result it is likely that construction and equipment associated with the latter technique will be lower with respect to complexity and costs.

With the above described mechanical means for product fabrication in view, the determinations of dimensions of cost effective products are given in the following section. This is followed by the section showing plant operations in the Process Flow Diagram.

# 6.1.1 Determination of the Dimensional Nature of Products

The dimensional nature of encapsulated waste products was estimated through determinations of their cost effective size. On the one hand, it is desirable economically to conserve resin employed for jacketing by encapsulating larger agglomerates. On the other hand, the expense concomitant with larger equipment and the additional time required to complete agglomerate formation counteract the advantage derived through reduced resin costs. Thus, the estimations of the size of products were related to thermal conductivity of the product which determines residence time in heating, required oven size, and the amount of required jacketing resin.

Heat transfer calculations were carried out on the molding and curing processes using the graphical solution of the three dimensional heat conduction equation.\* These calculations assume that the unfused agglomerate has a thermal conductivity of 0.4 Btu/hr ft<sup>2</sup>°F/ft and a specific heat of 0.2 Btu/lb°F. These values are typical of insulating materials and were utilized due to lack of data specific to this area. Oven sizes were calculated for three agglomerate block sizes, 500, 1000, and 2000 pounds,

Mc Adams, William H., <u>Heat Transmission</u>, 1954, Tosho Insatsu Printing Co., Ltd., Tokyo Japan

based on the heat transfer considerations. (The blocks were assumed to be cubes and the density based on two hazardous waste determinations was taken to be  $100 \text{ lbs/ft}^3$ .)

The required curing oven capacity increases as the block size increases since: (1) the time necessary to heat the block increases, and (2) the oven capacity increases in proportion to the residence time since the mass flow rate through the system is constant. The calculated cure time for various size blocks is presented in Figure 33. (The space between blocks was assumed to be constant at 1 foot.) Also, the required jacketing on a pound-per-pound of waste basis was determined for each of the three block sizes. Both of these parameters, oven size and pounds jacketing/1b waste, versus block size in pounds are shown in Figure 34. From this figure it appears that the optimum block size is approximately 1000 pounds, and is somewhat greater than two feet on edge. This conclusion is based on the following points:

- 1. The costs of oven and the jacketing are proportional to the size of the oven and the amount of jacketing material.
- 2. The oven size versus block size graph is nearly linear (i.e., constant slope for block size less than 1000 lbs). For block sizes greater than 1000 lbs the slope begins to increase and the curve appears to become exponential. Therefore, any block size less than 1000 lbs is acceptable with respect to oven size and the related cost.
- 3. The jacketing requirement versus block size is nearly linear for block sizes greater than 1000 lbs but approaches exponential form for block sizes less than 1000 lbs.

  Therefore, any block size greater than 1000 lbs is acceptable with respect to the jacketing.

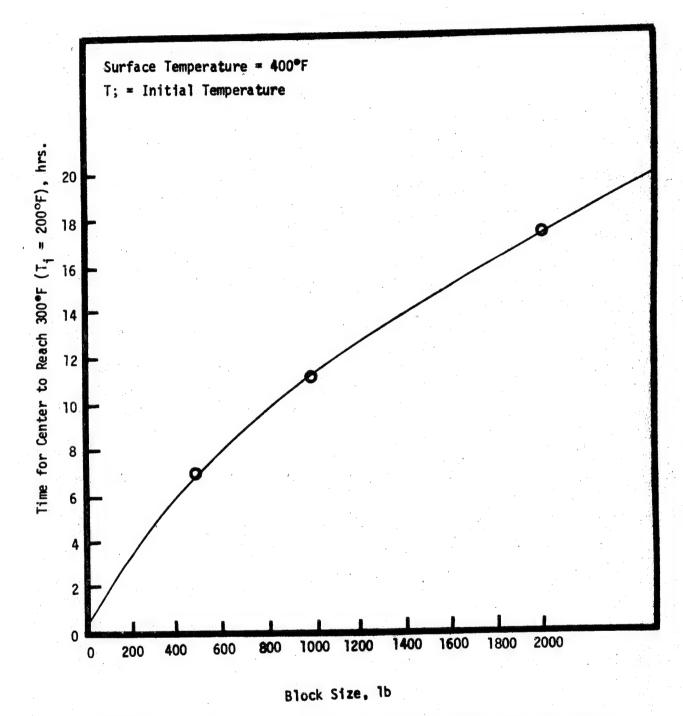


Figure 33. Time Required for Center to Reach 300°F as a Function of Agglomerate Size

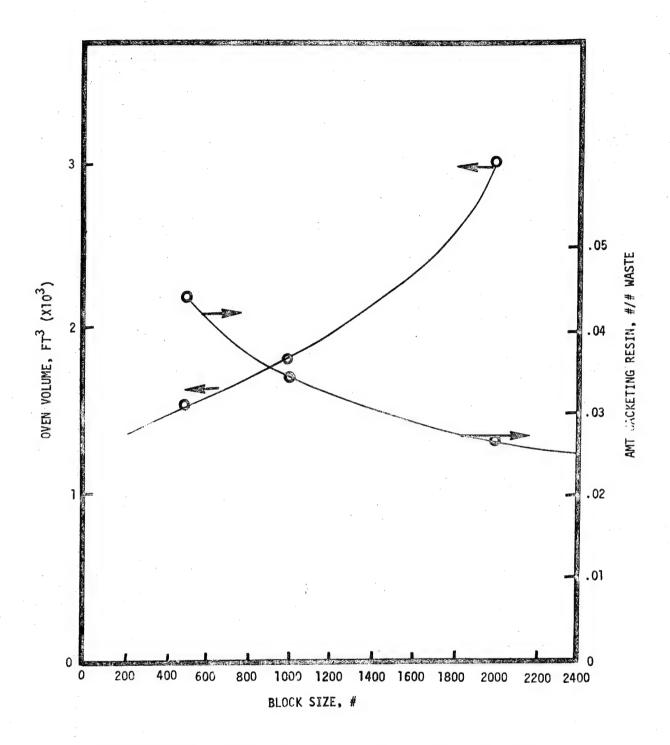


Figure 34. Oven Volume and Jacketing Resin Required as a Function of Agglomerate Size

4. From the points noted above, it is concluded that 1000 lbs is the optimum block size with respect to oven size and jacketing.

# 6.1.2 Process Flow Diagram

The process flow diagram for the encapsulation of solid hazardous waste is presented in Figure 35. The mass balances that are detailed later in Section 6.1.3 are presented alongside the flow diagram and are broken down into flow rates of the various components.

In the process, dry, particulated hazardous wastes are coated with a formulated polybutadiene solution. The solvent (acetone was employed in this work) facilitiates the coating of the particulates; subsequently, the solvent is evaporated and then condensed for recycle. The polybutadiene solution is prepared in the process by combining delivered, viscous polybutadiene liquid resin with solvent and additives.

An alternate method for preparing the polybutadiene solution is to polymerize butadiene in the solvent recovered from drying of the solution wetted wastes. This can be readily carried out by employing the Swarc synthesis method. In this method butadiene rather than viscous resin, would be delivered to the plant site. This method avoids the handling of viscous resins, an operation which may be awkward and costly.

The resin coated particulated wastes are agglomerated by heating and consolidation is complete when the center of the agglomerate reaches 300°F. The material is then uniformly hard. This consideration was employed in the process determination and cost estimations. It remains to be determined, however, whether consolidation to this extent is necessary in order to realize high performance products. If not, heating agglomerated wastes in ovens could be eliminated. The operation would be reduced to fusing compacted resin coated wastes at the surface of the compact. The resulting agglomerate would then be characterized by a stiff, tough surface encapsulating an unfused waste compact. Subsequently, the ensemble would be

resin jacketed by employing the mechanical means described previously. The processing scheme discussed in the following paragraphs utilizes liquid polybutadiene resins and curing ovens.

The dry waste is transported from storage to a pug mill by means of an enclosed conveyor belt. The storage for the waste consists of an underground silo with a hatch through which the silo is filled. To prevent dust from getting into the air and moisture from condensing in the silo, check valves to the bag filters and from the condenser are installed; hence, any exhausted air passes through the bag filters and any inleted air passes through the condenser. The pug mill coats the dry waste with the acetone-polybutadiene mixture. The acetone-polybutadiene is mixed in a closed tank using a propellor-type agitator. These components are pumped into the mixing tank from storage and recycled at a 5:1 acetone: polybutadiene weight ratio.

The coated waste is transported by a screw conveyor to the top of the rotary tray drier. The coated waste flows downward and is in contact with hot, rising nitrogen gas which evaporates the acetone completely from the coated waste. The nitrogen leaves the drier, flows through a bag filter which removes any particulates, and combines with vent streams from the pug mill and mixer into an acetone condenser. The liquid acetone is pumped to the mixer and the nitrogen is reheated using steam and is recycled (with make-up nitrogen added as needed) through the drier.

The solids (polybutadiene coated waste) leave the drier and are sent along with particulates recovered from the bag filters to the agglomerate mold. The residence time in this mold is about twenty-four minutes under slight pressure and a surface temperature of 400°F. Steam provides the necessary heat to effect curing of about three inches of the waste block.

The agglomerate block is transferred to the curing oven for about eleven hours to cure the block completely. Heating is accomplished by routing stack gases from the steam boiler to the oven. This gas is then exhausted to the atmosphere through a catalytic converter to remove any

organics. Jacketing the agglomerate is effected with powdered polyethylene as described previously yielding a five-side jacketed block. The partially coated (5 sides) block leaves the coating mold and is righted so that the uncoated surface is on top. The top surface is jacketed and the block is then sent to storage.

# 6.1.3 Mass and Energy Balances

Mass and energy balances around the pieces of equipment shown in Figure 35 were carried out to determine the amount of each component in the various streams. The mass balance is presented in Table 14. The assumptions used were:

- (1) 20,000 tons dry waste processed per year.
- (2) Density of the waste (compacted in mold) is 100 lbs/ft<sup>3</sup>:
  this is based on measurements of two hazardous waste samples.
- (3) Specific heat and thermal conductivity of the unfused wasteresin agglomerate is equal to that of insulating brick; hence,

$$cp = 0.2$$
 Btu/lb.°F  
 $k = 0.4$  Btu/hr·ft<sup>2</sup>.°F/ft

- (4) Temperature of process water for condenser is 80°F.
- (5) Acetone to polybutadiene ratio is 5:1 by weight.
- (6) Steam plant has efficiency of 70%.
- (7) Heat efficiency of agglomerate mold is 90%.
- (8) Surface temperature of waste agglomerate is 400°F during block formation.

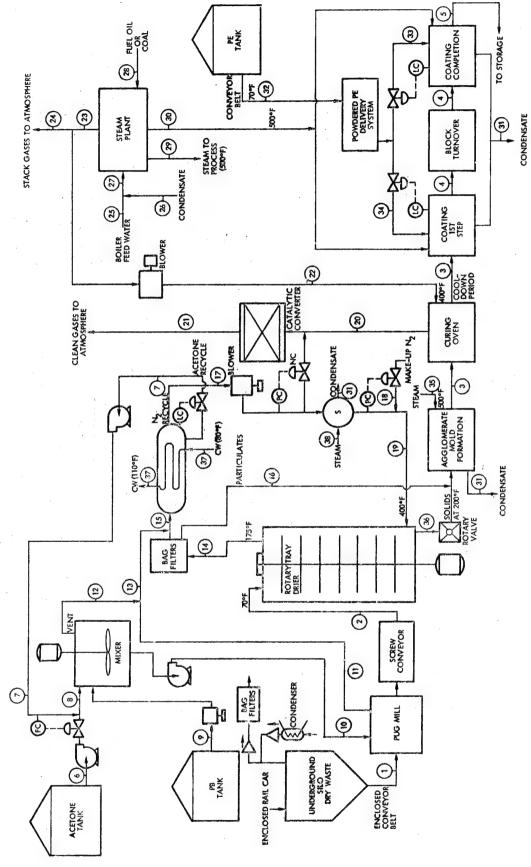


Figure 35. Process Flow Diagram

TABLE 14. MASS BALANCE

STREAM	_	2	%	3	. 4	5	. 9	7	8	6	10	11	12	13	14	15	91	17	81
FLOW, J/HR					·														
DRY WASTE	5051	5051	4951	5051	5051	5051									101	-	100	ı	
POLY BUTADIENE		8	136	138	156	135				951	156								
POLYETHYLENE					971	175													
ACETONE		756.6					_	794.8	8		88	23.4	91	39.4	2779	6442		5646	
NITROGEN															6475	6475		6469	17.1
PROCESS WATER			•																
BOILER FEED WATER																			
CONDENSATE																			
STEAM																			
FUEL OIL																			
STACK GASES																			
STREAM	61	20	17	Z	23	74	25	26	27	28	29	8	31	32	ಜ	ಕ	35	37	8
FLOW, 1/HR																			
DRY WASTE	-																1	:	
POLYMITADIENE													,						
POLYETHYLENE														175	8	4			
ACETONE	9795																		
NITROGEN	6481																		
PROCESS WATER							2											11,975	
BOILER FEED WATER							8.95		268										
CONDENSATE								986.4					895						
STEAM											198	34.4					121		740
FUEL OIL										51.82									
STACK GASES		195	195	561	97.6	365													

- (9) Temperature in curing oven is 400°F; efficiency is 90%.
- (10) Heat efficiency of drier is 90%; other losses in the drier system are negligible.
- (11) Heat losses in steam pipes negligible.
- (12) Blocks are cubes weighing approximately 1000 lbs (weight is actually slightly above 1000 lbs).
- (13) Polybutadiene concentration in blocks is 3% by weight.
- (14) Vent losses from mixer and pug mill are 2% and 3% respectively.
- (15) Solids leaving in nitrogen stream are about 100 lb/hr.
- (16) Efficiency of bag filters is 99%.

# 6.1.4 Equipment Costs

The installed equipment cost for the process was calculated using the technique presented by Guthrie. This method applies a "bare module factor" to the f.o.b. cost of the equipment to give the installed cost. Data from files, vendors, and other available sources was used to carry out these calculations. The results are presented in Table 15.

## 6.2 PROCESS ECONOMICS COMPUTER MODEL

The final task of the engineering effort was the development of the process economics model and an economic analysis of the process incorporating the model. This task is described below.

TABLE 15. INSTALLED EQUIPMENT COST

Equipment	Installed Cost, \$
Acetone Storage Tank (30 days)	5,400
Polybutadiene Storage Tank (30 days)	21,000
Waste Storage Silo (30 days)	132,000
Polyethylene Storage Tank (30 days)	24,000
Mixer (260 gallons, closed tank)	2,900
Pug Mill	70,900
Screw Conveyor	6,000
Rotary Tray Drier	433,000
Acetone Condenser (Shell and Tube)	10,000
Heat Exchanger (Double Pipe)	1,500
Bag Filters	12,900
Agglomerate Molds (2 required)	100,000
Curing Oven	30,000
Coating Mold	50,000
Block Turnover Mechanism	40,000
Coating Cap	15,000
Powdered Polyethylene Delivery System	206,400
Steam Boiler	22,000
Blower (stack gases to oven)	1,500
Blower (N <sub>2</sub> gas to drier)	2,700
Pump (acetone feed)	1,000
Pump (acetone recycle)	1,000
Pump (PB feed)	3,000
Pump (acetone/PB feed)	1,000
Enclosed Conveyor Belt (200 ft)	62,000
Conveyor Belt (stream 3-4; 500 ft)	75,000
Conveyor Belt (stream 4-5; 300 ft)	51,000
	TOTAL = $$1.38 \times 10^6$

A computer program was written in BASIC language to carry out an economic study of the encapsulation process. Parameters which can be changed to study their effect on the cost are: (1) size of the plant, (2) cost of the raw materials (3) percent polybutadiene binder used, (4) dewatering cost (associated with sludges), (5) equipment changes in the encapsulation process, and (6) the labor force. The program was written so that it can be used simply by following the instructions printed at the terminal.

The computer program was written such that the operator may make desired changes while in contact with the program. A logic flow diagram was drawn up prior to the actual writing of the program to insure that all options were included. This logic is presented in Figure 36 and the actual program listing which is based on the program logic is presented as Table 16. The initial data used in running the program are from the base case calculations. Each time the operator calls the program from disk storage, the data are read to insure that each variable has a nonzero value. The operator may then run the base case or change any parameter. Two options are available with respect to parameter changes: (1) S (plant size/base plant size), D (dewatering cost), and C(N) (raw material costs) may be changed simultaneously, or (2) any one of the six parameters previously listed may be changed individually. After the appropriate change is entered, the program initiates the necessary calculation scheme and prints out the results and value of each parameter. To assist the reader in understanding the program, a typical session along with an explanation of each step is presented in Table 17.

# 6.2.1 Parametric Studies

A series of economic evaluations was undertaken to determine the significant factors in the overall cost of the encapsulation process. A breakdown of the costs for the base case, which does not account for dewatering costs, showed that about 50% of the total cost was attributable to the raw material requirements, about 25% of the cost was attributable to the labor force requirements (assumed 5 positions per shift) and the remaining cost was associated with the equipment costs. The operating costs for the base case are presented in Table 18.

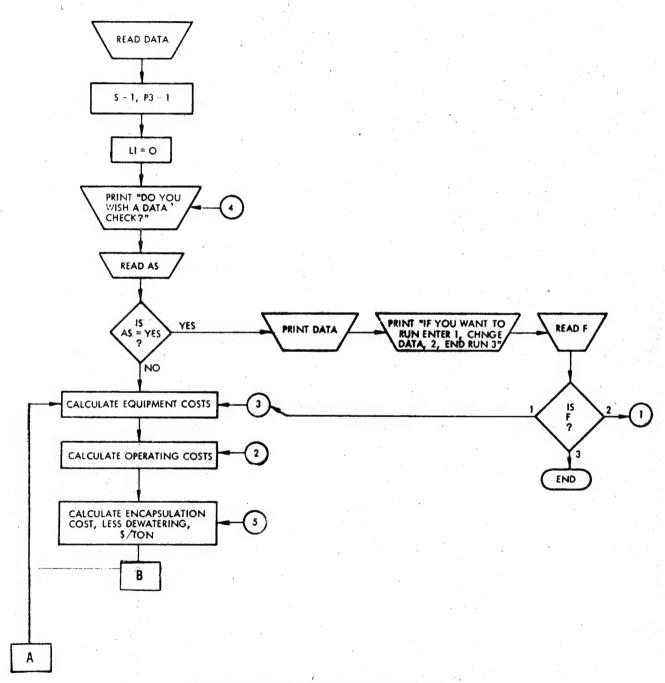


Figure 36. Computer Logic Diagram

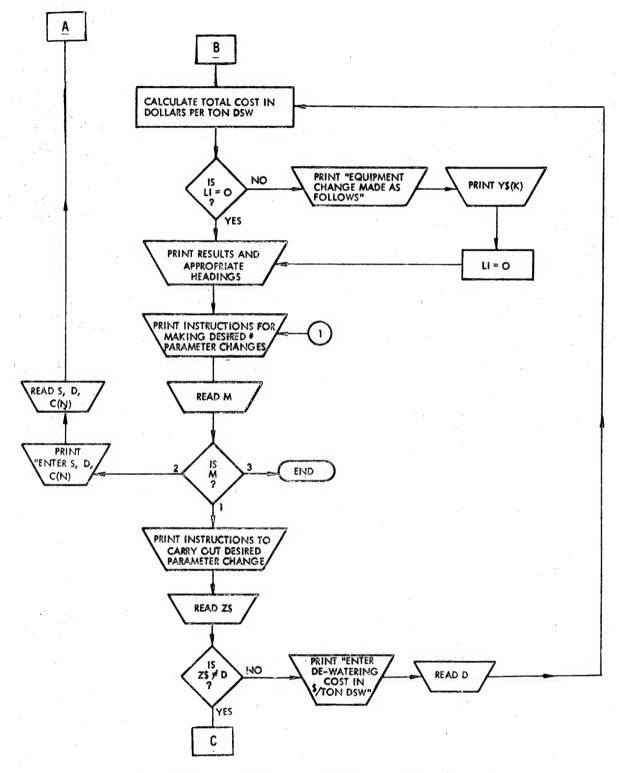


Figure 36. Computer Logic Diagram (Continued)

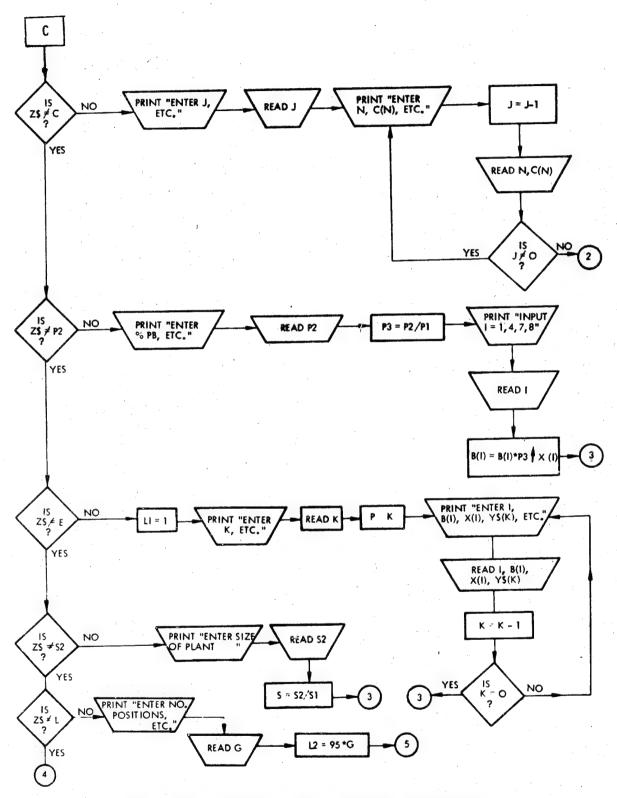


Figure 36. Computer Logic Diagram (Continued)

# TABLE 16. COMPUTER PROGRAM LISTING

```
1 VAR=ZERO
2 STRING AS, ZS
5 DIM B(20), X(20)
10 FOR I=1 TO 13
15 READ B(I)
20 NEXT I
25 DATA 182. 4, 29. 2, 3, 12. 4, 70. 9, 450, 2. 9, 245. 5, 65, 100, 12. 9, 3. 5, 200
30 REM B(I) IS BASE COST OF ENCAP EGMNT, K$; 4= SCREW CON, 13=MLTN PE DELIV.
35 FOR I=1 TO 13
40 READ X(I)
45 NEXT I
50 DATA •60, •70, •52, •75, •66, •45, •50, •65, 0, 1, •68, •85, •40
55 REM X(I) IS SIZE EXPNT; X(9)=0 IN ALL CASES FOR $2/$1.4.8.X(10)=1
60 FOR N=1 TO 4
65 READ R(N)
70 NEXT N
75 DATA 1.236E6, 1.386E6, 7.92E3, 1.228E6
80 REM R=AMT RAW MTRL, #/YR, BASE CASE; 1=PB, 2=PE, 3=ACETONE, 4=N2, SCF/YR.
85 FOR N=1 TO 4
90 READ C(N)
95 NEXT N
100 DATA 4.0E-4, 2.6E-4, 1.5E-4, 6.78E-6
105 REM C IS COST IN KS PER UNIT OF RAW MATERIAL
110 READ D. U.L. F1, F2, F3, S1, P1
115 DATA 5, 27.7, 475, 2.52, .04, .05, 20, 3
120 REM D=DEWTRING CST, $$/TON D.S.; U=UTILITIES CST, K$/YR; L=LBR CST, K$/YR
121 REM FI=FCTR OBTAIN MFG CAP FRM IEC; F2= FTRY INDRTS&MNTCE CST; F3=DEP
122 REM SIE BASE SIZE, KTONS D. S. /YR; PI= %PB IN AGGLOMERATE
125 S=1, P3=1
130 PRINT"DO YOU WISH A DATA CHECK?"
135INPUT AS
140 IF AS="YES" THEN 295
142 LET L1=0
145 LET T=0
148 FOR I=1 TO 13
150 IF S<4.8 THEN 160
152 IF I<>9 THEN 160
155 LET T=T+B(I)#2
157 NEXT I
160 LET T=T+B(1)*S*X(1)
168 NEXT I
165 LET MI=T+F1
170 M2=F2+M1.F4=F2+M1
175 LET D1=F3#M1
180 LET L2=L+S
185 LET U1=U*S
190 LET C1=C(1) *P3*S*R(1)
195 FOR N=2 TO 4
200 LET C1=C1+C(N)*S*R(N)
205 NEXT N
210 REM T=INST EQ CST, MI=MFG CAP, M2=MNT CST, F49F. I., DI=DEP, L2=LBR, UI=UTI
+ L, CI=RAW MAT CST
```

# TABLE 16. (CONTINUED)

```
215 LET W=(M2+F4+D1+L2+U1+C1)/(S#$1)
220 LET W1=W+D
225 IF L1=1 THEN 265
226 PRINT
227 PRINT
230 PRINT"RAW MATERIALS COST: PB, PE, ACETONE, NITROGEN, IN KS/BASE UNIT"
235 FOR N=1 TO4
240 PRINT C(N)
245 NEXT N
246 PRINT
250 PRINT"SIZE=": S*S1;"% PB=":P3*P1;"DEWATERING COST=":D;"LABOR=":L2
251 PRINT
255 PRINT"COST LESS DEWATERING, $/TON=", W, "COST, $/TON=", W1
256 PRINT
257 PRINT
260 GO TO 345
265 PRINT"EQUIPMENT CHANGE MADE AS FOLLOWS"
270 FOR K=1 TOP
275 PRINT YS(K)
280 NEXT K
285 LET L1=0
290 GO TO 230
295 FOR I= 1 TO 13
300 PRINT B(1), X(1)
305 NEXT I
310 FOR N= 1 TO 4
315 PRINT R(N), C(N)
320 NEXT N
325 PRINT D. U.L. F1. F2. F3. S. P3
330 PRINT"IF YOU WANT TO RUN ENTER 1, CHNGE DATA, 2, END RUN, 3"
335 INPUT F
340 ON F GO TO 145, 345, 610
345 PRINT"ENTER 1 FOR 1 PARAMETER CHNG, 2 FOR>1 CHNG, OR 3 TO END RUN"
350 INPUT M
355 ON M GO TO 390, 360, 610
360 PRINT "ENTER S. D. C(N)"
365 INPUT S.D
370 FOR N=1 TO 4
375 INPUT C(N)
380 NEXT N
385 GO TO 145
390 PRINT"WHICH PARAMETER DO YOU WANT TO CHANGE?"
395 PRINT"ENTER D FOR DEVATERING COSTS. C FOR RAW MATLS COSTS"
396 PRINT"P2 FOR X PB IN AGGLOMERATE, E FOF EQUIPMENT CHANGE"
397 PRINT"S2 FOR SIZE IN KTONS DRY WASTE THRU PUT PER YEAR"
398 PRINT'L FOR LABOR FORCE CHANGE"
400 INPUT ZS
405 IF Z$<>"D" THEN 425
410 PRINT"ENTER DEWATERING COST IN S/TON D. S. W."
415 INPUT D
420 GO TO 220
425 IF Z$<>"C" THEN 470
430 PRINT"ENTER J; J=NUMBER OF RAW MATLS COSTS TO BE CHANGED"
```

# TABLE 16. (CONTINUED)

```
435 INPUT J
440 PRINT"ENTER N AND C(N); N=NTH COMPONENT, C(N)=COST , KS/UNIT"
445 LET J=J-1
447 INPUT N
450 INPUT C(N)
460 IF J<>0 THEN 440
465 GO TO 190
470 IF Z$<>"P2" THEN 515
475 PRINT"ENTER 7 PB IN AGGLOMERATE; RECALC BASE COST EQ. I=1, 4, 7, 8"
480 INPUT P2
485 LET P3=P2/P1
487 PRINT"INPUT I=1, 4, 7,8 ON NEXT LINE"
490 FOR H=1 TO 4
495 INPUT I
500 LET B(1)=B(1)*P31X(1)
505 NEXT H
510 GO TO 145
515 IF Z$<>"E" THEN 560
517 LET L1=1
520 PRINT "ENTER K; K=NUMBER OF EQUIPMENT CHANGES TO BE MADE"
525 INPUT K
530 LET P≈K
532 PRINT"ENTER 1, B(1), X(1), Y$(K); I=ITH COMPNT, Y&=CHNG DESCPTN"
535 INPUT I
540 INPUT B(I), X(I), Y$(K)
545 LET K=K-1
550 IF K=0 THEN 145
555 GO TO 532
560 IF Z$<>"S2" THEN 585
565 PRINT"ENTER PLANT SIZE IN KTONS D. S. W. PER YEAR"
570 INPUT $2
575 LET S= $2/$1
580 GO TO 145
585 IF Z$<>"L" THEN 130
590 PRINT"ENTER NUMBER OF POSITIONS TO BE FILLED PER SHIFT"
595 INPUT G
600 LET L2=95*G
605 GO TO 215
610 END
```

# TABLE 17. SAMPLE COMPUTERS ECONOMICS SIMULATION

USER NUMBER:

```
. 4E-01
                                                                                                                                                                                                                                                                                                                                         RAW MATERIALS COST: PB.PE. ACETONE, NITROGEN, IN K$/BASE UNIT
                                                                                                                                                                                                                                                                                                                                                                                                        LABOR 475
                                                                                                                                                                                                                                                                             2.52
                                                                                                                                                                                                                                                                                                IF YOU WANT TO RUN ENTER 1, CHNGE DATA, 2, END RUN, 3
                                                                                                                                                                                                                                                                                                                                                                                                       DEWATERING COST= 5
                                                             S RIN
DO YOU WISH A DATA CHECK?
                                                                                                                                                                                                                                                                 678E-05
                                                                                                                                                                                                                                             . 26E-03
                                                                                                                                                                                                                                                       . 15E-03
                                                                                                                 52E+00
                                                                                                                           75E+00
                                                                                                                                     66E+00
                                                                                                                                                45E+00
                                                                                                                                                                    65E+00
                                                                                                                                                                                                   . 68 E+ 00
                                                                                                                                                                                                              85E+00
                                                                                                      7E+00
                                                                                                                                                          SE+00
                                                                                                                                                                                                                                  . 4E-03
                                                                                             • 6E+00
                                                                                                                                                                                                                        . 4E+00
                                                                                                                                                                                                                                                                            27.7
                                                                                                                                                                                                                                                                                                                                                                                                       M PB 3
SPL6.
                                         LOAD, BULL
                               GET, BULL
                                                                                                                                                                                                                                                                                                                                                                                   .678E-05
JOB NAME
                                                                                                                                                                                                                                                                                                                                                              .26E-03
                                                                                                                                                                                                                                                                                                                                                                                                       SIZE= 20
                                                    END LOAD
                                                                                                                                                                                                                                           1386000
                                                                                                                                                                                                                                                                 1228000
                                                                                                                                                                                                                                  1236000
                                                                                                                                                                                                                                                                                                                                                    • 4E-03
                                                                                                                                                                                                                                                                                      • 5E-01
                                                                                 7 YES
188.4
                                                                                                                                                                    245.5
                                                                                                                                                                                                                                                       7920
                                                                                                      29.5
                                                                                                                           12.4
                    BAS
                                                                                                                                     70.9
                                                                                                                                                                                                  12.9
                                                                                                                                                450
                                                                                                                                                                                                                       003
          PORT
                                                                                                                                                                                        100
                                                                                                                                                                                                             3.5
                                                                                                                                                                              65
                                                                                                                                                                                                                                                                                       OPTION TO RUN WITH
DATA AS PRINTED, CHANGE
DATA, OR EXIT FROM PROGRAM
                                                                            DATA CHECK OPTION
                                                                                                                                                                                                                                                                                                                                                                                      RESULTS
                                                                                                                                                                                     DATA CHECK RUIN
```

95.915418

CO ST. S/ TON=

90.915418

COST LESS DEWATERING, \$/ TON\*

OPTION TO CHANGE ONE OR MORE PARAMETERS OR END: ONE CHANGE SELECTED

OPTION TO PICK WHICH PARAMETER CHANGES

EQUIPMENT CHANGE OPTION

3 TO END RUN ENTER D FOR DEWATERING COSTS, C FOR RAW MATLS COSTS P2 FOR % PB IN AGGLOMERATE, E FOR EQUIPMENT CHANGE SE FOR SIZE IN KIONS DRY WASTE THRU PUT PER YEAR ENTER 1 FOR 1 PARAMETER CHNG, 2 FOR> 1 CHNG, OR WHICH PARAMETER DO YOU WANT TO CHANGE? L FOR LABOR FORCE CHANGE

7 E ENTER K; Kanumber of Equipment Changes to be made

ENTER I, B(I), X(I), YS(K); I=ITH COMPNT, Y&=CHNG DESCPTN ? 6,112,.45,LET DRIER COST EQUAL 25% BASE COST EQUIPMENT CHANGE MADE AS FOLLOWS LET DRIER COST EQUAL 25% BASE COST

RAW MATERIALS COST: PB, PE, ACETONE, NITROGEN, IN KS/BASE UNIT

· 26E-03 • 4E-03

.678E-05 • 15E-03

**RESULTS** 

LABOR= 475 S DEWATERING COST= က % PBm SIZE= 20 CO ST. \$/ TON= 85.378978 COST LESS DEWATERING, \$/ TON=

90.378978

ENTER 1 FOR 1 PARAMETER CHNG, 2 FOR-1 CHNG, OR 3 TO END RUN WHICH PARAMETER DO YOU WANT TO CHANGE? ENTER D FOR DEWATERING COSTS, C FOR RAW MATLS COSTS P2 FOR I PB IN AGGLOMERATE, E FOR EQUIPMENT CHANGE

IN KTONS DRY WASTE THRU PUT PER YEAR L FOR LABOR FORCE CHANGE

FOR SIZE

7 52 ENTER PLANT SIZE IN KTONS D.S.W. PER YEAR

SIZE CHANGE OPTION

RAW MATERIALS COST: PB, PE, ACETONE, NITROGEN, IN K\$/BASE UNIT

• 4E-03

.26E-03

.678E-05 • 15E-03

**RESULTS** 

LABOR 11875 DEWATERING COST= 5 5 mgc 2 SIZE= 500 CO ST. \$/ TON= 73.779451 COST LESS DEWATERING, \$/TON=

78.779451

82

# TABLE 17. SAMPLE COMPUTERS ECONOMICS SIMULATION (CONTINUED)

3	I N		2	RUN
O NO	ASE	75	<b>\$</b> / TC	EN D
3,08 3 10	EN. IN KS/E	LABOR= 475	CO 5T, \$/ TON=	3.0R 3 TO
ENTER 1 FOR 1 PARAMETER CHNG, 2 FOR-1 CHNG, OR 3 TO END RUN 7 E FNTER S, D, C(N) 7 1.50 ** 1.5	RAW MATERIALS COST: PB.PE.ACETONE.NITROGEN.IN KS/BASE UNI • 2E-03 • 13E-03 • 7E-04 • 34E-05	# PB= 3 DEWATERING COST= 50	COST LESS DEWATERING. \$/ TON- 63.770766	ENTER 1 FOR 1 PARAMETER CHNG, 2 FOR>1 CHNG, OR 3 TO END RUN
enter 1 FOR 1 7 E FNTER S, D, C(N) 7 1.50 #	FAV MATERI • 2E-03 • 13E-03 • 7E-04	SIZE 20	<b>WST LESS</b>	BNTER 1 FO
MORE THAN ONE CHANGE OPTION SELECTED	DECI.			END RUN

113.77077

TYPICAL SESSION: UNDERLINED PORTIONS ARE INPUT BY OPERATOR, OTHER STATEMENTS PRINTED BY COMPUTER.

LINE 00610 END

# TABLE 18. OPERATING COSTS - \$1000/YEAR

Utilities	27.7
Labor	475.0
Maintenance	139.0
Depreciation	174.0
Factory Indirects	139.0
Raw Materials	864.0
	1818.7

Cost = \$1818.7/20 = \$90.93/Ton

Cost = \$90.93/Ton

Cost <sup>↑</sup> \$91/Ton

Each of the parameters given in Section 6.2 was varied holding all other parameters constant to determine individual effects on the overall cost. To determine the relative effect of the parameters, a plot of the nondimensionalized operating cost (operating cost/base operating cost) vs nondimensionalized parametric values (value/base value) was constructed. Since the base cost of dewatering was taken as zero, the dewatering parameter could not be presented in this fashion. The graph (Figure 37) shows that increasing size will decrease cost; decreasing the values of the other parameters will also lower the cost. Raw materials cost (total) is shown to be the most effective means of lowering the operating cost; labor, equipment cost, and amount of polybutadiene in the agglomerate all have about the same effect on the operating cost. The following paragraphs deal with each study separately. It should be noted, however, that dewatering costs are not included except in the case where dewatering cost effects are examined.

The cost of encapsulation as a function of plant size, where size is amount of dry waste processed per year, was investigated for two cases:
(1) 3% polybutadiene binder, and (2) 5% polybutadiene binder. The results are plotted in Figure 38. The results show that the change in binder content had no effect on the shape of the cost vs size curve. The results

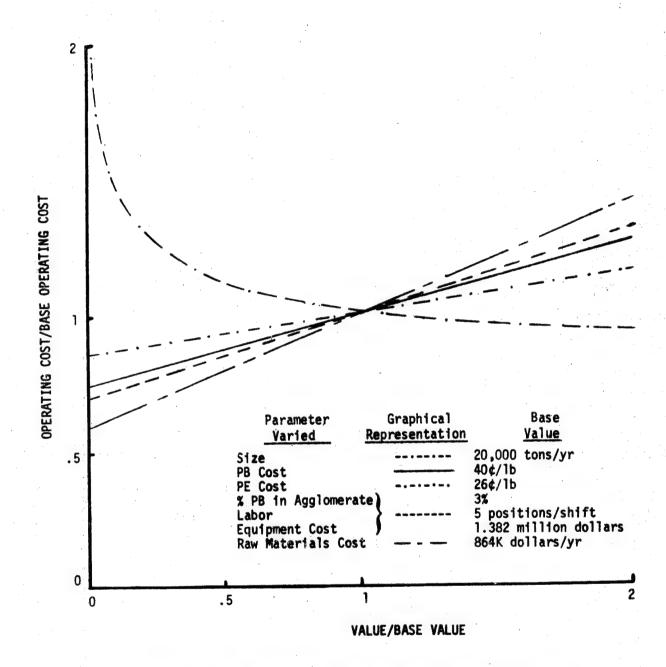


Figure 37. Comparative Effect of Parameter Changes on Operating Cost for the Encapsulation Process (Nondimensionalized Values Plotted)

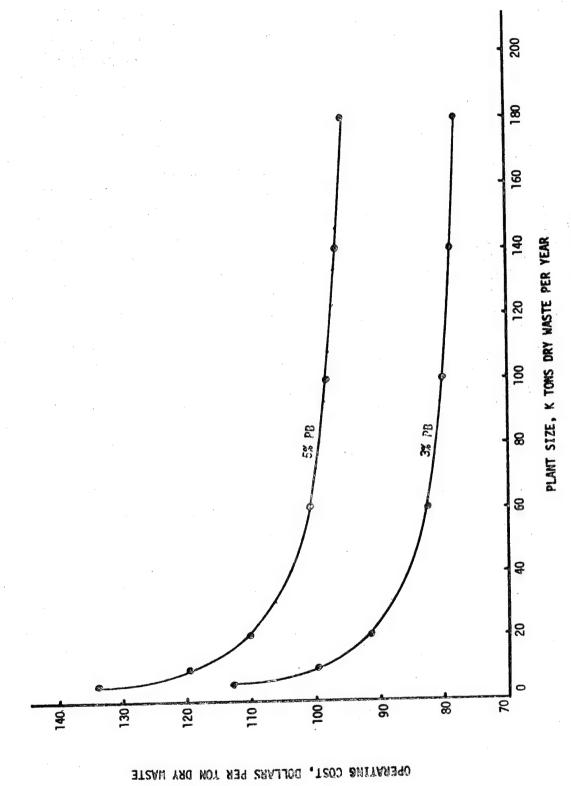


Figure 38. Operating Cost as a Function of Plant Size

also show that the plant should be sized between 20,000 tons per year and 60,000 tons per year. This range was arrived at because building a plant capable of handling more than 60,000 tons per year will not significantly reduce the cost of the process, and building a plant smaller than 20,000 tons per year causes a significant increase in cost.

Since the raw materials cost accounted for about 50% of the total cost (base case), a study of cost as a function of the individual raw material costs was undertaken. Preliminary results showed that the acetone and nitrogen costs were negligible; hence, only the polyethylene and polybutadiene costs were investigated. Results of the study are presented in Figures 39 and 40 for a process using 3% and 5% polybutadiene, respectively. For the 3% polybutadiene process, changing the cost of either material by the same amount changes the operating cost by nearly the same amount (PE has slightly larger effect). In the case of a process using 5% binder, however, the effect of changing the polybutadiene price causes a greater change in the operating cost than does an equivlent change in the polyethylene price.

Another point that was checked was the effect of the percent polybutadiene binder on the cost assuming a constant price (40¢/lb). Figure 41 presents the results which show that a decrease of 1% polybutadiene binder (i.e., 3% to 2%) in the agglomerate causes about a \$10 drop in the process cost. Of course, for lower priced material the effect is less.

The cost due to the labor force requirements was also studied. The base case assumed five positions per shift and an average rate of \$9.00/ hour. The results are shown in Figure 42 for a plant sizes of 20,000 tons per year and 100,000 tons per year. In the first case a charge of one position (equivalent to \$95,000/yr) results in about a \$7.25 change in operating cost, but for the second case this causes only a \$1.00 change in operating cost. Even if the labor force is reduced by the same percentage, the effect is still greater for the smaller plant.

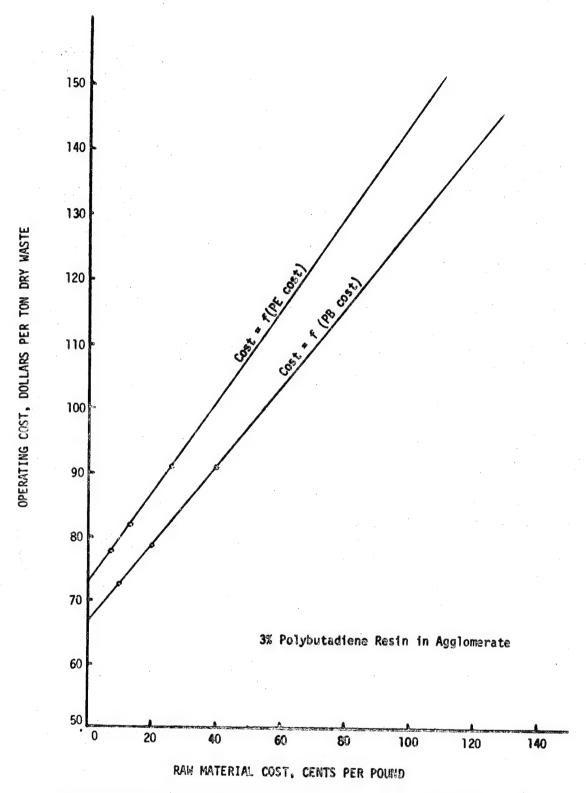


Figure 39. Operating Cost as a Function of Raw Material Costs

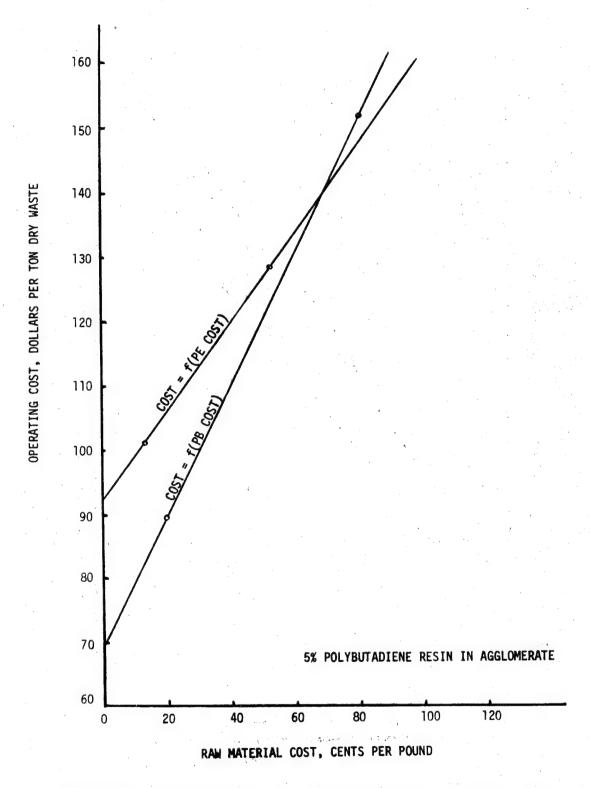


Figure 40. Operating Cost as a Function of Raw Material Costs

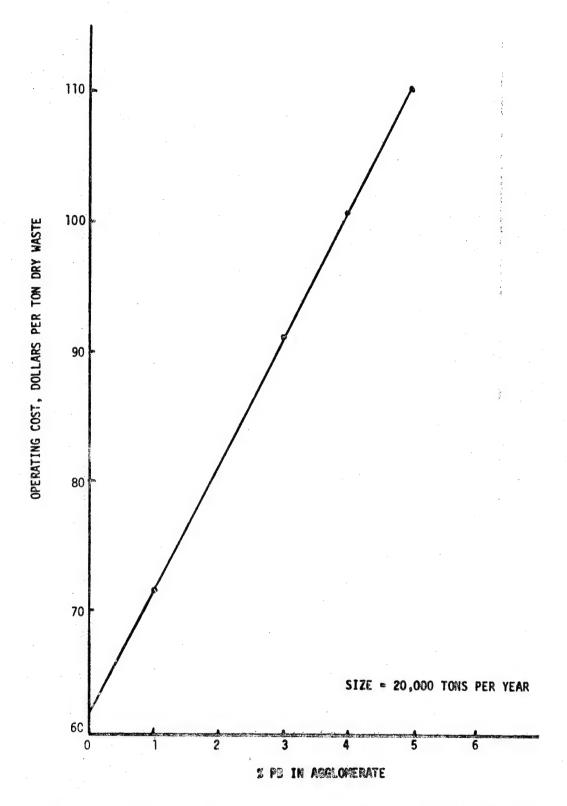


Figure 41. Operating Cost as a Function of % PB in Agglomerate

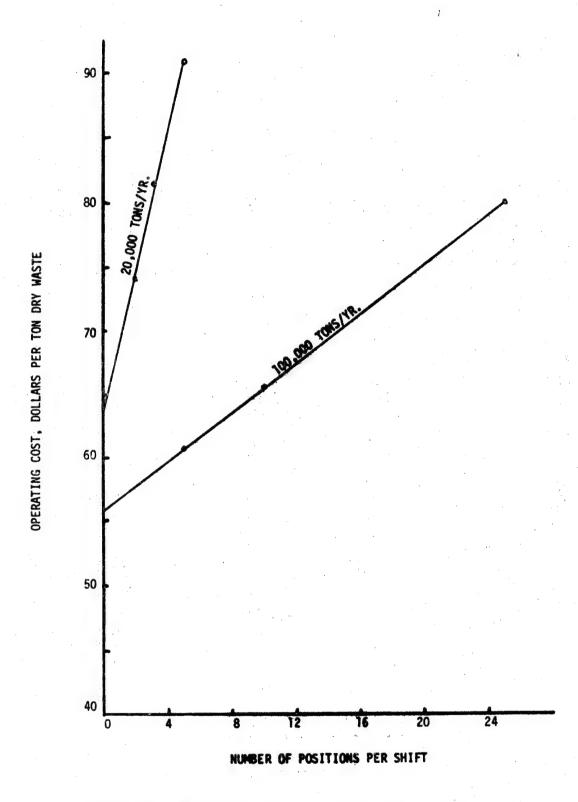


Figure 42. Operating Cost as a Function of Labor Force

Dewatering cost effects were studied as it was felt that not only solid wastes but also sludges might be handled by this encapsulation process. The literature indicated that the cost of dewatering tends to range from 6 to 20 dollars per ton of dry waste (1); therefore, this range was looked at and expanded. Since the dewatering in the literature deals with nonhazardous sludges, the costs are probably lower than would be encountered for handling sludges containing heavy metals. To fully analyze the dewatering cost a process needs to be developed and costed in a manner similar to the procedure used in arriving at encapsulation costs. The results presented in Figure 43 show that dewatering costs could account for as much as 50% of the total cost. It should be pointed out that the dewatering cost will be greatly dependent on the solids content; hence, streams containing high solids will cost less to dewater than streams containing low solids.

The parametric studies pointed out that small changes in raw materials cost (actual dollar values) have a significant effect on the change in operating cost. The size of the labor force needed will also have a significant impact on the cost of the encapsulation process. Equipment costs were not studied in depth since a substantial price reduction (actual dollars) is required to substantially reduce the operating cost. The area which appears to have the greatest effect on the operating cost is raw materials. Not only the price, but also the amount of these materials required, has a significant effect on the overall cost. A decrease in the binder content from 3% to 2% coupled with a price decrease of 10¢/pound would lower the operating cost by about \$12/ton dry waste. Therefore, primary efforts to decrease cost should be focused on the raw materials with secondary efforts aimed at decreasing equipment cost and labor force. The general conclusions of the economics study are as follows:

- Raw materials account for about 50% of the operating cost for encapsulation.
- Labor costs and factors associated with equipment cost each account for about 25% of the operating costs.

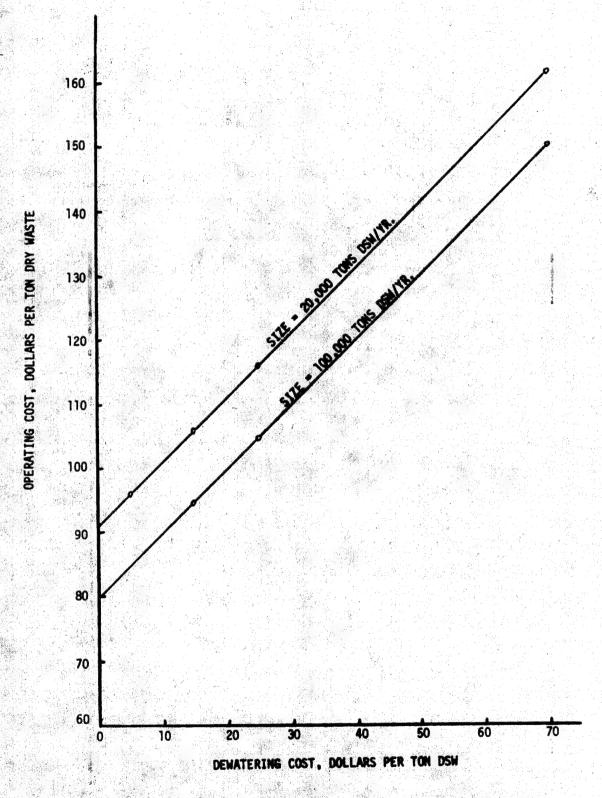


Figure 43. Operating Cost as a Function of Dewatering Costs

- Dewatering cost may be as high or higher than 50% of the total processing cost.
- An in-depth study of dewatering is required to determine the order of magnitude of this cost.
- Primary effort should focus on factors associated with raw materials in lowering operating costs; secondary efforts should be placed on labor and equipment cost.
- The capacity of the plant should be between 20,000 and 60,000 tons dry waste per year. In this size range costs do not vary significantly.

# 7. IDENTIFICATION OF MANAGEABLE WASTES

The purpose of this work element is to provide guidelines relative to employment of the TRW process for passivation of hazardous heavy metal containing wastes. In addition, estimates are given of the amount of heavy metals discarded by U.S. industry. Hazardous wastes are divided into three divisions: the first defining wastes for which the TRW process may be uniquely applicable; the second wherein higher passivation performance may be realized; and third, areas of application which require precaution in application of the TRW encapsulation method.

From the viewpoint of realizing high performance localization, certain hazardous, difficult to manage wastes destined for disposal into the ecological environment can be very effectively passivated, in our opinion, by the TRW process. (See Section 8 for further discussion.) Other, less hazardous, wastes currently passivated by incorporation in resin matrices (inorganic or organic material matrices) may exhibit stability only in a narrow range of environmental conditions. For such wastes, the TRW process, in our opinion, can assure higher performance localization under a broader range of exacting conditions than that of "matrix" passivation. Finally, some wastes exist for which the TRW process may not be applicable; in these cases, it may be necessary to test the process with respect to the specific waste.

The identification of difficult to manage wastes which are expected to be particularly applicable to disposal by the TRW process was related, as follows, to constituents present in the wastes. These consituents determine the suitability of passivation processes with respect to realizing high performance waste localization.

• The TRW process may be uniquely applicable to wastes containing, for example, sodium antimonide, sodium metaarsenate, sodium pyroarsenate, sodium arsenate fluoride, sodium chromate, sodium cyanide, sodium cyanocuprate, sodium fluoantimonate, sodium fluoberyllate, sodium fluoborate, sodium fluoride,

sodium iodide, sodium plumbate, sodium selenate, sodium selenide, sodium thiocyanate, sodium thioantimonate, lithium antimonide, lithium orthoarsenate, lithium fluoride, lithium iodide, lithium selenide, potassium antimonide, potassium orthoarsenate, potassium orthoarsenite, potassium cacodylate, potassium cadmium cyanide, potassium cynate, potassium cyanide, potassium cyanocadmate, potassium cyanocobaltate, potassium cyanocuprate, potassium cyanomercurate, potassium ferricyanide, potassium fluoberyllate, potassium hexofluorophosphate, potassium lead chloride, postassium magnesium selenate, potassium mercury tartrate. potassium selenate, potassium selenite, potassium selenocynate, potassium selenothionate, potassium sodium antimony tartrate, potassium thioarsenate, potassium thioarsenite, potassium thiocyanate, arsenic selenide, arsenic oxide. beryllium selenate, cadmium selenate, copper triarsenide, copper selenide, copper antimonide. lead orthoarsenate. mercury oxide, selenium oxide.

- The TRW process may advance the range of stability of wastes currently passivated in resin matrices containing, for example, arsenic bromide, arsenic disulfide, arsenic pentasulfide, arsenic trisulfide, beryllium acetate, beryllium bromide, beryllium fluoride, beryllium chloride, beryllium sulfate, beryllium acetate, beryllium carbide, cadmium pyrophosphate, cadmium metasilicate, cadmium sulfate, copper tetraammine nitrate, copper carbonate, lead acetate, lead bromide, lead chlorate, lead fluoride, lead phosphide, mercury bromide, mercury fluoride, mercury iodide, selenium chloride, selenium monobromide trichloride.
- The TRW process as presently constituted was applied to wastes free of mobile water and highly volatile compounds. The presence of absorbed water and organic matter, however, should not preclude the application of the process.

Organic matter containing mercaptans may affect the extent of resin reaction in agglomerate formation, however, it is most unlikely that sufficient mercaptan will be present to prevent rigidification of waste. This is due to the high functionality of the agglomerate binding resin wherein low extents of reaction will give rise to three dimensional structures. In the event agglomeration does not take place, flowers of sulfur in small quantities admixed into the resin should assure rigidification.

Sulfur curing was not employed in this work because it may, in our opinion, compromise ready demolding of the agglomerate after its formation. Demolding is a desirable property which facilitates waste passivation processing. Encapsulation of the resin agglomerated wastes, on the other hand, should not be effected by the chemical composition of the waste

In the preparation of encapsulated specimens in the laboratory, volatile matter in the agglomerate needed to be excluded in order to carry out effective encapsulation. Preparation of large, cost effective encapsulated waste products, described in Section 6, should not be sensitive to the presence of some volatile matter in the agglomerate. Thermal energy required for carrying out encapsulation heats only the extremities of the agglomerate, thus volatile matter produced will condense in the unheated bulk of the agglomerate.

Estimations of the quantity of heavy metals discarded by U.S. industry as waste is provided here. These estimations were based upon extracts of unpublished reports prepared in response to a program being carried out by the Office of Solid Waste Management Programs, U.S. Environmental Protection Agency, concerning an assessment of industrial waste practices. This program will provide reports reflecting waste generation and disposal

practices by industry as given in Table 19. The finalized reports will yield extensive information in respect to the nature and the amount of heavy metal waste produced by U.S. industry. Unfortunately, chemical compositions were not given of the compounds containing heavy metal atoms. Such information is desirable for assessing the utility and specificity of the TRW Process with respect to specific wastes.

The following paragraphs provide information concerning heavy metal wastes from industries designated by the paragraph titles:

#### 7.1 METAL MINING

The wastes of metal mining usually consist of overburden, waste rock, and tailing. These materials do not contain toxic materials concentration greater than the land in which they are disposed. Thus they do not contribute generally to the potential hazards.

Ore concentration, however, can give rise to "tailings" which may contain toxic substances in higher concentrations than the land on which they are disposed. Of particular concern is pyrite (FeS<sub>2</sub>) due to its formation of sulfuric acid in the presence of air and water. The acid could then leach toxic metals from the waste. Of further concern are tailings from the uranium industry, (SIC 1094) the lead/zinc industry (SIC 1031), and the copper industry (SIC 1021). These tailings contain the following heavy metals: Copper, lead, zinc, cadmium, radium, arsenic, selenium and beryllium. Adequate waste treatment and land-disposal methods for potentially hazardous wastes, however, were reported to be available to the metal mining companies.

### 7.2 INDUSTRIAL INORGANIC CHEMICALS

The nature and amount of heavy metal wastes stemming from the inorganic chemical industry are given in Table 20. About 12000 metric tons (0.6 percent of the total) go into secured landfill. On-site storage and disposal such as deep welling, currently accounts for over 75% of the total waste

## TABLE 19. INDUSTRIES CURRENTLY UNDER STUDY

1. Industry: Metals Mining

SIC Codes: 1021; 1031; 1092; 1094; 1099 Contractor: Midwest Reserach Institute

Completion: February 1975

2. Industry: Industrial Inorganic Chemicals

SIC Codes: 281

Contractor: Versar, Inc. Completion: November 1974

3. Industry: Pharmaceuticals

SIC Codes: 283

Contractor: A.D. Little, Inc. Completion: February 1975

4. Industry: Paint and Allied Products

SIC Codes: 285

Contractor: WAPORA, Inc. Completion: February 1975

5. Industry: Organic Chemicals, Pesticides, and Explosives

SIC Codes: 286, 2879; 2892 Contractor: TRW Systems Group Completion: February 1975

6. Industry: Petroleum Refining

SIC Codes: 291

Contractor: Jacobs Engineering Company

Completion: December 1974

7. Industry: Primary Metals

SIC Codes: 331; 3321; 3322; 3324; 333; 3341; 3399

Contractor: Calspan Corporation

Completion: January 1975

8. Industry: Electroplating

SIC Codes: 3471

Contractor: Battelle Columbus Laboratories

Completion: February 1975

9. Industry: Primary and Storage Batteries

SIC Codes: 3691; 3692 Contractor: Versar, Inc. Completion: November 1974

TABLE 20. SUMMARY OF LAND DESTINED HAZARDOUS WASTES FROM INORGANIC CHEMICAL INDUSTRY (SIC 281) (DRY BASIS)

	45)	Metric <u>Current</u>	Tons/Year to 1977	Land Disposal
SIC 2812	Hazardous Constitu <b>ents (1</b>	) 7,000	7,500	4,200
	Total Waste Stream	57,000	56,000	45,000
SIC 2813	Hazardous Constituents (2 Total Waste Stream	) o o	0	0 0
SIC 2816	Hazardous Constituents (3	4,700	5,800	6,900
	Total Waste Stream	160,000	230,000	320,000
SIC 2819	Hazardous Constituents (4) Total Waste Stream	52,000 1,800,000	53,000 2,000,000	66,000 2,400,000
	Hazardous Constituents	64,000	66,000	77,000
	Total Waste Stream	2,000,000	2,300,000	2,800,000

<sup>(1)</sup> From Alkalies and Chlorine Industry; asbestos, chlorinated hydrocarbons, lead, mercury.

<sup>(2)</sup> From Industrial Gases Industry; no hazardous constituents.

<sup>(3)</sup> From Industrial Pigments Industry; antimony, arsenic; cadmium, chromium, cyanide, lead, mercury, zinc.

<sup>(4)</sup> From Industrial Inorganic Chemicals; arsenic, fluoride, chromium, nickel, phosphorus.

generated by the industry. Since treatment/disposal costs were reported to be a relatively low percentage of the product selling price, more effective means of waste localization may be employed with respect to improving performance and, perhaps, without impacting adversly upon product price.

#### 7.3 PHARMACEUTICALS

Table 21 gives the nature and the amount of heavy metal wastes generated by the pharmaceutical industry.

TABLE 21. ANNUAL HEAVY METAL WASTES GENERATED BY THE PHARMACUETICAL INDUSTRY

Waste Type	Waste Lbs/year	Heavy Metal in Wastes Lbs/year
Zinc	5,000,000	2,000,000
Arsenic	1,000,000	20,000
Chromium	50,000	20,000
Copper	10,000	3,000
Selenium	400,000	1,000
Mercury	1,500	600

Source: ADL, Inc. Estimates

Most of the hazardous wastes are organic in nature and are disposed by incineration. Heavy metal containing residues may not be readily recycleable economically, therefore localization is required for their passivation.

#### 7.4 PAINT AND ALLIED PRODUCTS

Hazardous wastes which could stem from the paint and allied products industry contain arsenic, beryllium, cadmium, chromium, copper, lead, mercury, selenium, zinc. The first eight elements are materials which EPA believes, on the basis of initial analysis, to have the potential for producing serious public health and environmental problems. The contractor added the following elements with toxic chemical potential: antimony, barium, and cobalt. With respect to the above list of heavy metals no plant surveyed was found to employ arsenic and beryllium.

### 7.5 ORGANIC CHEMICALS, PESTICIDES, AND EXPLOSIVES

No appreciable amount of heavy metal wastes was found to stem from the organic chemicals industry.

#### 7.6 PETROLEUM REFINING

Wastes generated from the petroleum refinery industry as sludges, solids and slurries are estimated to be 1.3 million metric tons per year. In 1977 and 1983 the projected estimates are 1.4 million and 1.5 million metric tons per year, respectively. The proximate analysis of the aggregate waste has a moisture content of 59%, an oil content of 8%, and an ash content of about 33%.

The total amount of hazardous constituents is approximately 250 metric tons/year (dry basis). Chromium and zinc represent 62% of all potentially hazardous constituents found in the refinery total. Copper, nickel, vanadium, and lead are the next four highest constituents in terms of total amounts of potentially hazardous waste representing 29%. These four additions to chromium and zinc account for 90% of the total weight of hazardous constituents.

## 7.7 PRIMARY METALS

The principal potentially hazardous constituents found in primary and secondary smelting residuals are heavy metals, including arsenic, cadmium, lead, zinc, copper, chromium, antimony, and nickel. Because of trace amounts in the concentrates and ores from which the metals are recovered, the primary base metal smelting and refining industries (i.e., lead, copper, zinc, antimony, mercury, tungsten, and tin) produce a wider variety of heavy metals in residues, including arsenic, cadmium, lead, zinc, copper, antimony, nickel and mercury.

The predominant practices used in the primary and secondary non-ferrous smelting and refining industries for disposal of residuals are lagooning and open dumping. Slags and other solid residues are generally open dumped on land. Scrubwater from wet emissions control and process wastewater with or without lime treatment is generally routed to unlined settling pits or to unlined lagoons. Settled sludge is often dredged from pits or lagoons and stored or disposed of on land. Industries which produce relatively small quantities of sludge will often leave sludges permanently in lagoons The use of unlined settling pits and lagoons is the predominant practice.

Although the presence of potentially hazardous constituents in slags sludges and dusts has been shown, it is generally not known if these materials are leached in disposal environments. In the event that significant leaching is demonstrated, a number of recommendations are made with respect to practices for adequate health and environmental protection. It is suspected that sludges and dusts may leach heavy metals and other potentially hazardous constituents to a greater extent than most slags because of fine particle size and consequent susceptibility to weathering processes.

#### 7.8 ELECTROPLATING

Table 22 provides an estimate of total national waste from electroplating and metal finishing.

TABLE 22. ESTIMATED TOTAL NATIONAL WASTES FROM ELECTROPLATING AND METAL FINISHING JOB SHOPS, METRIC TONS PER YEAR (72 HOUR WEEK BASIS)

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Degreaser Sludge	5,579.69
Water Pollution Control Sludge	57,864.76
Other Solid Waste	118,348,27
Total	181,792.72
1977	
Degreaser Sludge	5,579.69
Water Pollution Control Sludge	109,163.88
Other So' Waste	118,348.27
Total	232,616.10

Metal hydroxides found in sludges are: Fe  $(OH)_2$ , Cu  $(OH)_2$ , Zn  $(OH)_2$ , Ni  $(OH)_2$ , Al  $(OH)_3$ , Cr  $(OH)_3$ , Cd  $(OH)_2$ , Sn  $(OH)_2$  and Pb  $(OH)_2$ .

#### 7.9 PRIMARY AND STORAGE BATTERIES

Large quantities of lead, cadmium, zinc, and mercury are used in battery manufacture and thus appear in the wastes produced by the industry, though they are present in only 5% of the wastes destined for land disposal and in low concentrations. The amounts of heavy metals which are reported by the U.S. Bureau of Mines (1973) for battery production in the U.S. are 698,038 kkg lead (50% of U.S. consumption), 848.3 kkg cadmium (15% of U.S. consumption), 408.2 kkg mercury (22% of U.S. consumption) and 27,210 kkg zinc (20% of U.S. consumption).

The land destined wastes from the battery industry contain a small percentage of heavy metals compared to the industry's total consumption. Only 0.007% of the total lead used by these industries is lost as waste, while 0.3% of the total cadmium, 0.5% of the total mercury, and 1.5% of the total zinc are lost.

The storage battery industry (SIC 3691) currently disposes of 47.3 kkg of potentially hazardous constituents on land in a total waste stream of 9,235 kkg consisting of water effluent treatment sludges and rejected and scrap cells. Projections for 1977 for land disposal indicate that these figures will grow to 467 kkg of hazardous constituents contained in a total waste stream of 162,800 kkg. By 1983, land disposal of hazardous wastes will increase to 625 kkg in a total waste stream of 207,700 kkg.

The greatest amount of wastes destined for land disposal from this industry stems from lead-acid battery production. A large increase in hazardous waste for 1977 and 1983 is projected on the basis of future wastewater treatment guidelines. These projections are based on information obtained from industry on future growth of the industry along with possible changes in the wastewater treatment area, which will affect the amount of wastes destined for land.

The primary battery industry (SIC 3692) currently disposes of 448 kkg of potentially hazardous constituents in a total waste stream of 1,202 kkg; the waste consists primarily of rejected and scrap cells, together with water effluent treatment sludges and furnace residues. By 1977, projections indicate that 514 kkg of hazardous constituents in a total waste stream of 1,500 kkg will be destined for land. By 1983, projections indicate that 502 kkg of hazardous constituents in a total waste stream of 1.350 kkg will be land disposed. The decrease of wastes going to land from 1977 to 1983 is due to projections concerning recovery of valuable scrap from the waste stream and a projected decrease in hazardous wastes from mercury cell production.

The wastes from battery production are generally not water soluble, and would normally have only minimal migration in a landfill environment. However, solubility varies greatly with small changes in pH, and pH varies in soils, groundwaters, and necessarily in landfill environments. For this reason those wastes containing heavy metals in any form or concentration have been considered potentially hazardous due to the possibility of leaching into surface or groundwater.

The prevalent method of treatment and disposal for potentially hazardous wastes from the storage batteries industry is land storage of wastewater treatment sludges and reclaimation, where possible, of reusable
heavy metals such as lead, nickel and cadmium scrap. The best available
technology currently used for the wastes from this industry is a segregated
landfill equipped with leachate collection and treatment. Disposal in
secured landfills is considered an environmentally adequate level of technology for small volume wastes with a relatively large hazardous waste
content. Disposal of large volume sludges with a lower hazardous waste
content in approved disposal facilities, with leachate treatment and
monitoring, is also considered environmentally adequate.

For the primary batteries industry, the prevalent method of treatment and disposal is in a simple landfill. The best available technology currently used for the wastes from this industry is segregated landfill equipped with leachate monitoring. Disposal in secured landfill is considered an environmentally adequate technology for the small volume, relatively high levels of hazardous wastes from this industry.

The cost of disposing of the small volume wastes in secured landfills does not appear to have significant economic consequences to the industry. The only area where relatively large costs are involved is the disposal of calcium sulfate water treatment sludges containing lead from the lead-acid storage battery industry.

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# 8. FURTHER OBSERVATIONS

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This work showed that the TRW process for passivation of dry, heavy metal waste may be employed generally without need to tailor the process with respect to the nature of the waste. When the passivated wastes were subjected to a broad range of exacting leaching solutions, all the heavy metal wastes investigated in this study exhibited high performance localization. Similar results should be expected for other heavy metal wastes as well.

Certain heavy metal wastes, in our opinion, can not be successfully passivated by means other than the TRW process. Such wastes would contain, or could yield with certain compounds, heavy metal atoms in the anionic moiety of salt compounds wherein the counter ions are alkali metals. Such compounds are usually very soluble in water. In the anion, heavy metals usually exist in chemical conjunction with other atoms as coordination complexes, thereby realizing electron saturation of their electron orbitals. Consequentially, it is not possible to fashion the insoluble coordination complexes with selected resins that would give rise to stable localization of heavy metals in resin matrices without prior chemical treatment of the contaminants. The effectiveness of most current passivation processes in this respect may be questionable because they depend upon the formation of such complexes.

Furthermore, the TRW process may be uniquely applicable to other types of wastes. Such wastes would contain water insoluble heavy metal salt and covalent compounds. Although these wastes resist heavy metal dispersion into the ecology by dissolution, they may be subject to such dispersion in particulate form by ecological forces. Encapsulation, in our opinion, may be the most effective means for precluding such occurrences.

Resins can be tailored, however, to passivate heavy metals when such metals exist as cations of salt compounds. Heavy metal cations in many such cases contain electron orbitals which give rise to stable coordination

complexes with certain resins, e.g., polysilicic acids. Yet even here high performance localization may exist only in a narrow range of environmental chemical conditions.

Although it would be desirable to rate heavy metal wastes with respect to their receptibility to passivation by different passivation processes, the lack of knowledge concerning the nature of the heavy metal compounds in the waste, and the complexity of the wastes per se, percludes such a rating. In our opinion, however, all heavy metal compounds without respect to their chemical state, with the possible exception of those yielding gaseous compounds, would be effectively localized by the TRW process. Nevertheless, certain wastes may be more suitable to localization by other means when relating heavy metal waste passivation to a cost-performance framework.

The mechanics of processing and the materials required determine the cost of products stemming from the TRW process. An estimate of \$91 a ton was provided. This estimate was based upon processing and materials in a large scale operation that follows the operation as carried out in the laboratory. But in this work the laboratory operation was directed to fashioning specimens for performance evaluations, and not to determining means for reducing costs. Yet it is meaningful to estimate the initial cost in this fashion because it relates cost to products whose performance have been characterized. Additional work should be directed to decipher means for reducing costs, and this work will, in our opinion, yield meaningful economic gain while maintaining production of high performance products.

Agglomeration, for example, can be effected by thermally hardening the resin coated waste merely at the faces of the agglomerate rather than throughout. Thus, partial hardening, which can occur in the mold, may be sufficient to carry out subsequent, effective resin jacketing of the agglomerate. Wastes with volatile matter will be more readily processable because the volatiles would readily condense in the innards of the agglomerate rather than being vented into the atmosphere. The ovens shown in the work for hardening agglomerates throughout could be eliminated.

The commercial resins employed in this work are resins of quality in advance of that required for fashioning high performance products. Crude polybutadiene resin for making agglomerates, in our opinion, are sufficient; and the higher cost, electrical grade, commercial resin, employed here for convenience sake, is not necessary. The use of lower grade resin should make a significant impact on price due to the greater costs associated with production of electrical grade resins. Lower grades of commercial polyethylene may also be employed for jacketing agglomerates, although greater care may be required when compromising the resin quality of polyethylene than that of polybutadiene. However, low cost filler and resin extenders may be employed for reducing cost without sacrificing product performance.

#### CONCLUSIONS

This work concerning organic, polymeric cementation and encapsulation of hazardous wastes (TRW process) led to the following conclusions:

- Cementation of particulated solid waste containing heavy metal contaminants such as Cu, Cr, Zn, Ni, Cd, Hg, and As, and other metals such as Na, Ca and Fe can be readily carried out with polybutadiene resin yielding agglomerates having 94 to 97% by weight waste.
- Agglomerates can be securely encapsulated with 1/4 inch thick polyethylene jackets by fusing powdered polyethylene onto agglomerate surfaces, yielding passivated hazardous waste.
- Passivated hazardous waste, experimental products prepared in the laboratory by the TRW process exhibit excellent retention of hazardous contaminants in leaching by a broad spectrum of aqueous solutions.
- Products show high compressive strengths and withstand freeze-thaw and mechanical impact.
- A cost effective, high performance product would be characterized as follows: dimensions, cubic, approximately two feet on edge; weight, in the range 800 to 1000 pounds; jacket, about 1/4 inch thick polyethylene resin; encapsulated hazardous waste agglomerate cemented by 3 to 6% by weight polybutadiene resin, and jacketed by about 4% w/w polyethylene resin. Total resin required is about 8% w/w.
- Passivation costs are estimated to be about \$91 per ton in a processing operation yielding 20,000 tons per year.\*

<sup>\*</sup>Costs are based upon price of virgin resins vended by resin producers.

- Resin costs account for more than 50% of the product production costs.
- Difficult to manage wastes designated for disposal in landfill, deep well, etc., were assessed to be amenable to successful localization by the TRW process, such wastes containing, for examples, sodium metaarsenate and arsenic trisulfide.
- High performance localization of waste may be maintained by TRW process products under ambient conditions more varied and severe than those which define the limits of stability of wastes passivated by current means employing resins or waste "fixation" additives.
- The TRW process exhibits general applicability in passivation of dry particulated waste, i.e., no prior treatment of waste nor adjustment of the process is required.

#### RECOMMENDATIONS

Fabrication of commercial application scale prototypes is required in order to carry out chemical and mechanical characterization of cost effective products. This information is necessary for correlating performance of laboratory test specimens with that of full-scale products. Thus a more complete and accurate picture is provided for product performance under service conditions.

The agglomerated test specimens fabricated in this study from resin coated, particulated contaminants were "hardened" thermally throughout so that equivalent products would be realized for comparative evaluation purposes. The need for such thorough hardening is questionable, in our opinion, for realization of high performance of encapsulated waste. Yet production costs were based upon such a procedure because it was desirable to base the costs upon application scale products which approximate the test samples fabricated and characterized in the study. By producing products having a partially cured agglomerate where the surface and the region immediately below is characterized by particulates fused hard and the interior by material exhibiting a rubbery consistency rather than products having an agglomerate that is thoroughly hardened, it would be possible to markedly advance the rate of production of products. It also may be possible to eliminate certain items of capital equipment.

Within the framework of the above considerations, additional application scale prototypes are required for chemical and mechanical characterization. With such information in hand, the product fabrication procedure should be restructured in order to minimize production costs consistent with high product performance.

Finally, prototypes should be fabricated with impure and scrap resins. For the sake of convenience and the constraints of the study, virgin, commercial resins were utilized. In our opinion, an impure cementing resin would be very satisfactory in formation of agglomerates. Although the quality of resin employed for encapsulating the agglomerate should not be

compromised significantly, the cost of this material may be reduced by use of resin fillers and extenders. Fortunately, room for greater latitude in resin quality lie in the higher cost cementing resin. Thus significant impact upon product production costs could be realized by employing lower cost resins yet maintain high product performance.

In summation, advancement of this work requires:

- Evaluation of full-scale prototypes.
- Investigation of prototypes with agglomerates surface hardened to various depths.
- Examination of the utility of products fabricated with impure and scrap resins.

#### APPENDIX A\* - ORGANIC RESIN ENCAPSULATION

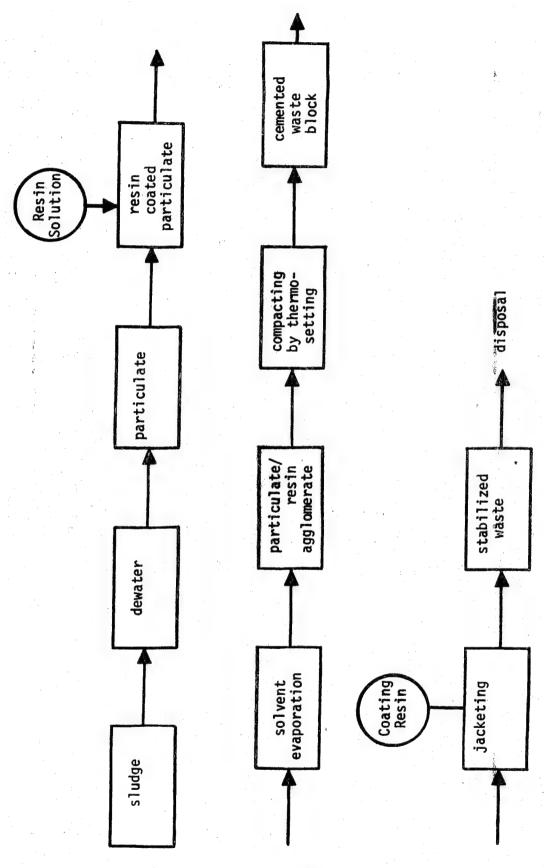
#### INTRODUCTION

The purpose of passivation is to limit the release of hazardous waste components to acceptable levels. Since water is usually both the solvent and the transport medium for wastes disposed to the land, the most effective techniques for effecting passivation are expected to be those which best isolate the wastes from water. Plastics have particular appeal for this application because of the well known aversion most plastic systems have for water.

Early efforts with plastic systems involved mixing the waste materials with molten plastics which solidify upon cooling. The high viscosity of the molten plastics generally limited the quantity of waste that could be loaded into the plastic matrix. The incorporation method was also limited by the inability of the matrix to isolate the waste from the environment. A highly loaded matrix exposed some waste at the surface of the block directly to the environment where it could be leached. Leaching exposed further surface area and so forth.

The TRW organic cementation process differs considerably from the simple incorporation or one step techniques tested previously. The TRW technique is a "two step" process which involves mixing the waste with an unfinished prepolymer, curing the polymer to a finished plastic, then jacketing the resulting agglomerate in order to isolate it from the environment. This procedure uses significantly less resin than the previous technology (95+% loadings as opposed to 30% loadings) and furthermore, the hazardous materials are better isolated from the environment by a uniform coating rather than the random packing typical of the "one step" method. The organic cementation process involves three basic operations as shown in Figure A-1: (1) coating the solid particulates with a prepolymer dissolved in an organic solvent, (2) compacting the particulate/ prepolymer system into a block by application of pressure and curing (thermosetting) the thermoset resin with heat, and (3) jacketing

<sup>\*</sup>From work performed under Contract No. 68-03-0089



Schematics of Organic Cementation Process for Stabilization of Hazardous Wastes Figure A-1.

(encapsulation) the resin cemented waste block with coating resin by fusion.

In the remainder of this section the various process studies made during this phase on the organic cementation technique are discussed. The selection of resins for the matrix and jacket is described. The experimental efforts on both the core and jacketing are also discussed in the following: SELECTION OF ORGANIC RESINS FOR AGGLOMERATION OF SOLID WASTE PARTICLES

In the selection of resins suitable for agglomeration of solid particulates the following criteria were applied:

- High loading ability, i.e., small amounts of resin must be capable of agglomerating and cementing large amounts of waste particulates.
- Chemical stability of the agglomerate waste.
- Ability to readily wet solid waste particulate.
- Easy and rapid formation of resin coated waste agglomerate for a wide variety of waste materials.
- Uniform distribution of resin in the agglomerate.
- High heat distortion temperature (HDT) to allow for wide selection of resin for jacketing; fusion of coating resin to the cemented waste core should not cause any dimensional distortion of the compacted core block.
- Low cost.
- Stability under normal conditions: no special precautions for resin storage.
- Satisfactory fluidity of waste/resin agglomerate particulates for fast and thorough filling of mold for compacting by thermosetting.
- Long "pot life" to allow the processing time to vary widely.

Since they can be formulated to meet all of the above criteria hydrocarbon resin systems are excellent binders for passivation of heavy metal compounds by agglomeration and thermosetting cementation. They are non-polar and provide a resinous matrix for embedding the waste particulates. The heavy metal salts are not soluble in the hydrocarbon resins and consequently they affect neither their rhelogical properties nor the chemical reactions which occur during thermosetting.

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Within the general category of hydrocarbon resin systems certain of the polybutadiene resins appear particularly attractive for cementation of hazardous waste particulates. Butadiene, the monomer from which the resins are synthesized, is a major product of the petrochemical industry. It is readily available and relatively low in cost and is expected to remain so despite the shortages of petroleum. Butadiene is a major component of rubber tires and therefore must remain a commodity chemical.

The monomer polymerizes to yield polybutadienes of various stereo configurations depending upon the conditions of polymerization. Polybutadienes of certain configurations were found to be unsuitable for use as agglomerate binders. The unstabilized high 1,4 cis, and high 1,4 cis/trans materials were found to be susceptible to oxidation under atmospheric conditions.

The high 1,2 stereoregular, and high 1,4 trans are solids melting at high temperature. The polybutadienes found to be particularly applicable for agglomerate formation were those with stereoconfigurations high in 1,2 atactic. These materials are liquid and they polymerize easily because of the high content of unsaturated bonds.

Atactic 1,2 polybutadiene resins without chemically functional groups can be synthesized as polymers of relatively low molecular weight, i.e., about 1000 to 2000. They are quite fluid when heated to temperatures of about 320°F, the temperature required to bring about rapid thermosetting of the resin. This fluid state, unfortunately, contributes to resin drainage in the course of transition of the compacted waste to the agglomerated state. Consequentially, the resulting agglomerates may not exhibit uniform distribution of waste in cross section.

Two methods may be used to decrease the fluidity of the polybutadiene resins during thermosetting. One is to utilize polybutadienes of substantially greater molecular weights. The other is to utilize polybutadienes of similar molecular weights which contain chemically functional terminal groups. The latter approach was selected in this work since it combines high fluidity at the time of initial resin coating of the waste with reduced fluidity during thermosetting.

The chemically functional polybutadienes selected for this work were those containing carboxyl groups. Hydroxyl groups and mercapto groups were also considered. The advantage of the carboxyl groups was that they are readily attached, react with epoxide resins to reduce fluidity during thermoset and are stable in air. The mercapto groups react with epoxide resins but they are labile under atmospheric conditions. The hydroxyl groups are oxidatively stable, but they do not react readily with the epoxide resins. Hence, both mercapto and hydroxyl groups were discounted in this work.

Epoxide resin (for viscosity control) was added to a solution of carboxylterminated polybutadiene containing a small amount of catalyst peroxide for use in resin thermosetting. A small amount of organic base was also added in order to promote the desired linear extension of the polybutadienes through the carboxyl-epoxy reaction. This solution was found to have excellent shelf stability. The resin coated wastes were made by solution wetting of the waste, followed by evaporation of the solvent. They were also found to have excellent shelf stability and excellent "pot life" so long as the material was not exposed to sunlight for prolonged periods.

# SELECTION OF ORGANIC RESINS FOR JACKETING

Jacketing or encapsulation of the agglomerated waste/resin core with a layer of coating resin is designed to separate the core content from environmental forces which might disperse the toxic components into the environment. The resins selected for jacketing must meet certain requirements; the most important are:

- Resistance to water
- Chemical stability
- Thermal and mechanical stability
- Good adhesion to the jacketed waste core
- Easy processability onto the surface of the core
- Low cost
- Non-biodegradable
- Resistant to weathering

Three resins meeting the above criteria were utilized in the jacketing experiments:

- Polyvinyl chloride plastisols (PVC) are liquid and may be readily fashioned into thermally stable material by heating.
- Polybutadiene modified epoxides produced by Goodrich Rubber Company. Preliminary experiments indicated that upon altering of the rheological properties of these resins good coatings may be obtained.
- Polyethylene resins treated with polybutadiene resin (PE/PB). The polyethylene particles coated with functional polybutadiene resin yielded a more homogeneous coating which exhibited upgraded thermal stability, mechanical strength and diffusion resistance. The combination of chemically functional polybutadiene with polyethylene is a unique and novel plastic system developed during this work.

#### EXPERIMENTAL ORGANIC CEMENTATION STUDIES

# Experimental Studies on Compacting of Solid Particulates into Blocks by Cementation with Resins

Feasibility studies on the applicability of the organic resins for cementation of solid particles were usually performed using sodium chloride as a waste simulant. The hazardous waste simulant used for the inorganic testing was also used for some tests. The procedure for agglomeration of solid particles was as follows:

the constituents of the cementing resin were dissolved in a solvent, usually acetone (the amount of solvent by volume was about 4 times the volume of resin). The solid particles were mixed with the resin solution in a Hobart mixer. After intimate blending the solvent (acetone) was evaporated with gentle heating leaving behind resin covered agglomerates of solid particles. These agglomerates were transferred into detachable rectangular aluminum molds. There, the agglomerate was squeezed with a plunger under low pressure, the plunger was removed and the agglomerate in the mold was heated to 350°F for 30 minutes. The agglomerate consolidated into a block of cemented solids due to thermosetting of the resin. After removal from the mold the warm block was ready for jacketing.

The various organic cementation experiments are summarized in Table A-1. Various resin systems were formulated and applied to the test solids. As shown in the result summary the formulations were applied in varying proportions to the solids. Since limiting the amount of resin while achieving satisfactory performance would keep costs down, the studies were concentrated in the range of 93 to 99 percent solids excluding solvent. For example, in experiment 1 five different solids loadings were examined over the range from 95 percent solids (5 percent resin) to 99 percent solids (1 percent resin).

An interesting and important feature of the solids/resin systems is the free-flowing consistency of the resin coated solid particles (Figure A-2). This characteristic allows for fast and uniform filling of the mold. The cemented block, however, is a very stable structure (Figure A-3).

Experimental Studies on Jacketing Cemented Blocks With Organic Resins

Jacketing with polyvinyl chloride plastisol: in general, the jacketing
was performed using commercial polyvinyl chloride plastisol in dioctyl
phthalate (DOP) solution, (Brand PK 5581A\*). For a coating thickness of
1/8 inch the curing conditions are 350°F for a half-hour. Thicker coatings

were cured at 400°F for a half-hour.

<sup>\*</sup>Product of Chemical Product Corporation, Western Division, Burbank, California.

TABLE A-1. ORGANIC CEMENTATION EXPERIMENTAL RESULTS

Kesin Formulation	Weight	Material	of Resin	Conditions	Results
Carboxyl terminated 1,2 polybutadiene MM ~1000 ("Hystl" C-1000) <sup>a</sup> Epoxy resin (Epon 828) <sup>b</sup>	e 100 21	sodium chloride	3 2 -	350°F 30 min	Weak, brittle Selfsustaining Good
Dicumyl peroxide (Di-Cup R) <sup>C</sup> Benzyldimethylamine (BDMA)	5.1.		4. ru		Good
Hydroxyl terminated polybutadiene "Hystl" G2000 p.pl-diphenylmethane diisocyanate Triethylene diamine (TEDA) Dicumylperoxide (Di-Cup R)	100 34 0.135 5.36	sodium	N w et n	200°F 30 min and 350°	Selfsustaining Good Good Good
Polybutadiene ARCO Tolumme diisocyanate (TDI) Dicumyl peroxide (Di-Cup R)	7.0 7.0	sodium chloride	~\n≪\n	350°F 30 min	Brittle Selfsustaining Good Good Good
Polybutadiene "Hystl" G2000 Toluene diisocyanate (TDI) Dicumyl peroxide (Di-Cup R)	2.7. 8.7.	sodium chloride	<b>-</b> , 2	350°F	Block fell apart Block fell apart
Carboxyl terminated 1,2 polybuta- diene NM 1000 "Hystl" C1000	8	solid waste	in .	350°F 30 min	<b>D</b> 009
Epoxy resin - Epon 828 Dicumyl peroxide (Di-Cup R) Benzyl dimethylamine (BDMA)	21 5.1 0.6		7		900g

Distributed by Dynachem Corp., Santa Fe Springs, California

Bisphenol A - Epichlorohydrin, produced by Shell Chemical Corp.

c Hercules Inc., Chemical Dept.

d General Mills Chemical Co. or Mobay Chemical Corp.

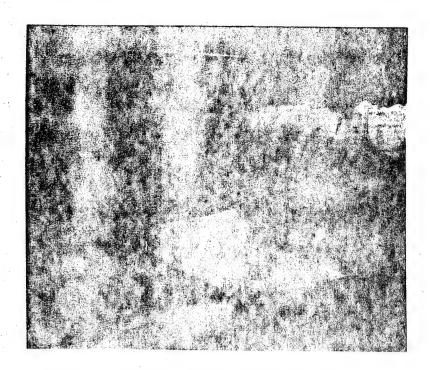


Figure A-2. Solid Waste Particles Coated with Polybutadiene Resin.

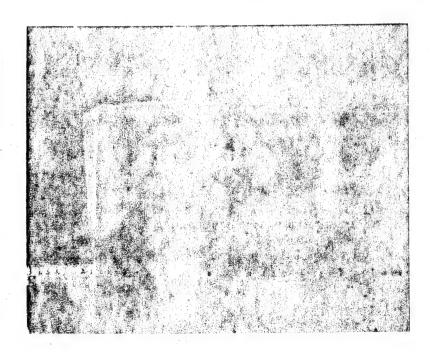


Figure A-3. Solid Waste Specimens Cemented with PB Resin: Left Uncoated; Right Coated with PVC

Agglomerated blocks were jacketed by placing them in a metal mold and pouring resin into the annulus. The jacket was fashioned in a two-stage operation; in the first stage approximately 5/6 of the surface area was covered. The resulting partially coated block rested upon the jacketed surface while additional resin was thermally fused onto the uncoated area. The two-stage operation allowed venting of any residual volatiles that may be present in the block prior to the completion of the jacketing procedure. The seam at the juncture contact of the first and second stage jacketing was found to be tough and flaw-free. Such results were expected because usually a given resin adheres to itself. The blocks jacketed with PVC plastisols were found to demold easily. No sticking or crumbling was observed. A freshly removed block and its mold are shown in Figure A-4.

A cross section of a jacketed block, shown in Figure A-5, exhibits the interface between the jacket and the agglomerate. The jacketing resins partially penetrated into the agglomerate. Mechanical locks were formed between the jacket and the agglomerate.

Figure A-6 shows cemented sodium chloride blocks jacketed with PVC resin before and after application of a compression stress of about 1000 psi. Although yielding in accommodation to the highly distorted cemented block, the jacket did not undergo break or rupture.

Jacketing with polybutadiene/epoxide resins: Goodrich Chemical resins consisting of polybutadiene treated epoxides were evaluated as jacketing resins. These resins yield tough flexible products. The presence of polybutadiene in their compositions imparts desirable chemical as well as mechanical locking of jackets onto the surfaces of the agglomerated wastes. The properties of the jacket can be readily varied through judicious formulation of Goodrich resin compositions. In this work, the Goodrich resins became quite fluid at the jacketing fusion temperature and penetrated appreciably into the body of the salt-containing agglomerate. They did not yield "neat" resin jackets. It is expected that this could be controlled given further study.

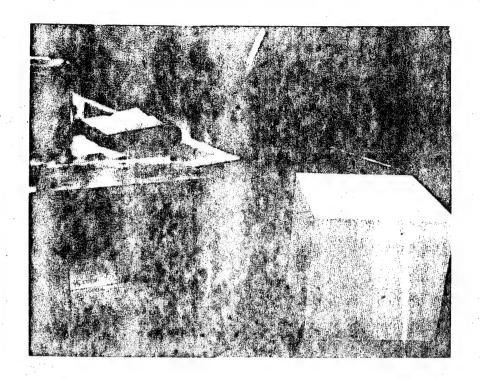


Figure A-4. Mold and Freshly Removed Waste Block

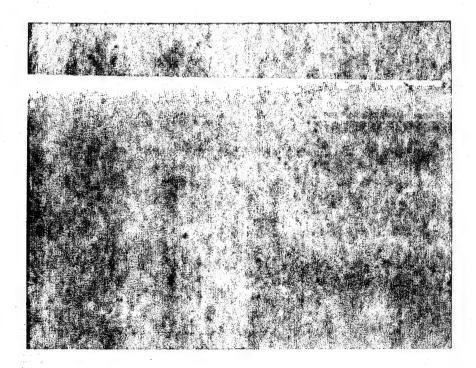


Figure A-5. Interface of Jacket and Block Showing Partial Penetration of Plastic Jacket into the Aggregate Block

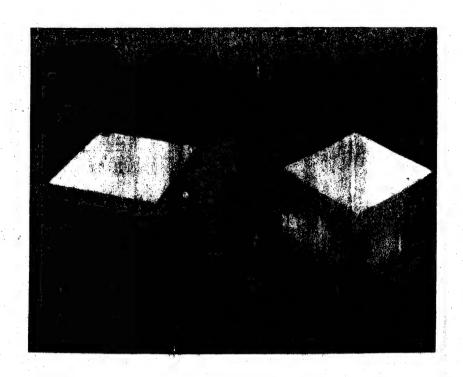


Figure A-6. Dimensional Distortion of Jacketed Agglomerates Under High Unidirectional Mechanical Loads

Jacketing with polyethylene resins: a thermoplastic resin, polyethylene, was investigated for use as a jacketing material. Powdered polyethylene sold by U.S.I. under the trade name Petrothene was used in the experimentation.

The powdered thermoplastic was tamped into the annulus between the block and the metallic mold. Simple application of heat was found not to cause intimate knitting of the powdered resin into a homogeneous jacket. Consequently, a metallic tube was machined and inserted into the annulus. Mechanical pressure was applied by this tube during heating of the resin yielding homogeneous jackets.

The final application of the thermoplastic resin in the two-stage jacketing procedure was accomplished by thermally fusing additional resin while cooling the other surfaces onto the agglomerate. Mechanical pressure was again applied through a metal rod. A product stemming from these operations is shown on the left side of Figure A-7.

The purpose of modifying the polyethylene with polybutadiene was to advance the dimensional stability of polyethylene at elevated temperatures. In order to realize tough, homogeneous, high performance products, various polybutadiene-polyethylene formulations were investigated. The composition shown in Table A-2 provided the most satisfactory results.

The modification of polyethylene with polybutadiene resin was performed in acetone solution. Liquid polybutadiene resin was dissolved in acetone. Polyethylene powder and other additives were added and the composition was mixed. The acetone was evaporated. The polyethylene powder coated with polybutadiene resin was compacted and fused under pressure at 320°F onto the cemented solid block. The procedure assured chemical as well as physical bonding of the jacketing resin with the jacketed core. The jacketing composition maintained rigidity to 350°F (the highest temperature tested) after fusion. At this temperature unmodified polyethylene was found to flow as readily as a molten candle wax. Excellent protective jackets were obtained in this way. A specimen jacketed with polyethylene resin modified with polybutadiene is shown on the right hand side of Figure A-7.



Figure A-7. Polyethylene Jacketed Agglomerated Solids. Left: Polyethylene Jacket. Right: Polybutadiene Modified Polyethylene Jacket.

TABLE A-2. POLYBUTADIENE-POLYETHYLENE COMPOSITION

Parts by Weight
100
21
5
0.6
570

While the coating on the right has a milk white, waxy appearance, the one on the left is translucent. This effect probably stems from the loss of polyethylene crystallinity due to the presence of the thermoset polybutadiene within the resin composition.

#### **ENVIRONMENTAL TESTING**

Cementation and encapsulation of hazardous wastes prior to ultimate disposal is designed to prevent or limit the dissipation of toxic elements or their compounds into the environment for an indefinite period. In order to anticipate the behavior of the cemented and coated hazardous solid wastes and sludges in ultimate disposal environments, laboratory prepared specimens were subjected to a series of tests. The test program was designed to provide preliminary data as to the expected behavior of the encapsulated wastes when subjected to environmental stress. Of particular interest was the ability of the encapsulated material to resist mechanical attack, such as, crushing and attack by aqueous solutions. Major stress was placed on the qualitative behavior of the systems therefore, quantitative modelling of the results was not attempted. The chemical analysis were designed to detect the ions of interest in the 1 ppm regime. This corresponds to losses of mass to the cemented blocks of the order of one-thousandth of a gram. Since the experiments are not directly correlated to actual environments no conclusions can be drawn as to toxicity implications.

Mechanical Testing: the mechanical testing of cemented uncoated and coated specimens included the determination of: (a) bulk density, (b) surface hardness, and (c) compression strength. The bulk density was determined by dividing the weight of the specimens by their bulk volume. The surface hardness was determined using Type D durometer, Pandux, Model 307 which conforms to ASTM D 1484 and ASTM D 1706.\* The compression strength was determined on the testing machine "Cal-Tester."\*\*

<u>Visual Observation</u>: the visual observation of the uncoated and coated specimens included examination under the microscope of the specimens

Produced by Pacific Transducer Corporation, Los Angeles, California.

\*\* Produced by Pacific Scientific Company, Anaheim, California.

before and after leaching. Particular emphasis was placed on the interface boundary between cemented waste specimens and coating. For this purpose the coated specimens were crosscut after leaching.

Leaching Experiments: the leaching of each specimen was conducted in 750 ml of aqueous solution at room temperature. The solutions were agitated mildly twice a day and prior to withdrawing of samples in order to eliminate concentration gradients. Accidental contamination of the leaching solutions was prevented by wrapping the tops of the beakers with plastics. The following leaching solutions were used:

- Distilled water
- Saturated carbonic acid; CO<sub>2</sub> bubbling at a rate about 60 ml/min. Approximate pH ~3.8 - 4.0.
- 0.1M sodium sesquicarbonate solution ( $Na_2CO_3/NaHCO_3$ ). Approximate pH  $\sim$ 10.1.
- Landfill leachate simulant having the following composition:

Sodium acetate	4.0 g/1
Potassium acetate	3.5 g/l
Ammonium acetate	3.0 g/l
Calcium acetate	30.0 g/l
Magnesium acetate	3.0 g/l
Ferric chloride	3.0 g/l
Sodium nitrate	0.1  g/1
Tannic acid	2.0 g/1
Glucose	2.0 g/1

<u>Leachate Analysis</u>: the leachates of the mainstream of uncoated and coated specimens were analyzed after 1, 2, 4, 8, 15, 22, 30 and 60 days of leaching.

The physico-chemical testing of the leachate included the determination of pH and the determination of the specific conductance. Chemical analyses determined the concentration of the toxic elements: As, Hg, Se, Cd, Cr, Pb for those samples containing these elements or the concentration of Na for the cemented sodium chloride compacts.

The analytical procedure consisted of the following steps: 1) all solutions were mechanically mixed prior to removal of a 25 ml sample, 2) this 25 ml was then replaced with de-ionized water, the pipet rinsed and the next sample taken, and 3) one ml of concentrated HNO<sub>3</sub> was added to each solution as a preservative and in addition all samples were refrigerated if there was a significant time delay between sampling and analysis.

The elemental composition was determined by atomic absorption (AÅ). The operating parameters are summarized in Table A-3. AA standards were made using the neat extraction solutions. This was done to minimize any inherent magnification or suppression of the analytical signal due to matrix effects.

TABLE A-3. ATOMIC ABSORPTION OPERATING PARAMETERS

Element	Flame Conditions	Analytical Wavelength Å	Slit Width Å	Lower Limit of Detection (ppm)
Na	Air-acetylene	8890	4	0.01
Hg	Air-hydrogen	2536	10	5.0 <sup>a</sup>
As	Argon-hydrogen	1937	4	0.3
Se	Argon-hydrogen	1960	10	0.5
Cr	Air-acetylene	3529	4	0.06
Cd	Air-acetylene	2288	4	0.02
Pb	Air-acetylene	2833	4	0.3

By using a flameless technique this value can be reduced to 0.01 ppm. However, the time required for the analysis is significantly higher.

# ENVIRONMENTAL TESTING OF ORGANIC CEMENT SAMPLES

The following  $2 \times 2 \times 2$  inch specimens were used in environmental testing:

- Sodium chloride cemented with 2% by weight of polybutadiene resin.
- Sodium chloride cemented with 3% by weight of polybutadiene resin.
- Sodium chloride cemented with 4% by weight of polybutadiene resin.
- Sodium chloride cemented with 5% by weight of polybutadiene resin.
- Sodium chloride cemented with 5% by weight of polybutadiene resin and coated with polyvinyl chloride plastisol.
- Hazardous simulant cemented with 7% by weight of polybutadien resin.
- Hazardous simulant cemented with 7% by weight of polybutadiene resin and coated with polyvinyl chloride plastisol.
- Sodium chloride cemented with 5% by weight of polybutadiene resin and coated with polyethylene/ polybutadiene coat.

The sample preparation followed the methodology described in Section 2.

## Testing of Sodium Chloride Compacts Cemented With Polybutadiene Resin

Table A-4 presents the mechanical properties of uncoated sodium chloride compacts cemented with different amounts of PB resin. The data refer to the specimens not subjected to leaching. The compression strength and hardness of these specimens was very good. After leaching of parallel specimens for 60 days in water they lost about 70% of their sodium chloride content, became lighter than water and floated on it. The concentration of sodium chloride in water was about 18%, i.e., approximately 50% of the saturation value. After removal from the leaching solution the specimens appeared very soft. The water, which replaced the sodium chloride at leaching, could be squeezed out. No mechanical testing was possible on these specimens at this stage.

Table A-5 presents the mechanical properties of sodium chloride compacts cemented with 5% PB resin and PVC coated following removal from leaching solution. The compression strength of the specimen coated with polyvinyl chloride after leaching is satisfactory. A parallel specimen before leaching exhibited compression strength 714 psi, i.e., 2-1/2 times greater. The compression strength of the PE/PB coated specimen was excellent before and after leaching, in excess of the range of the testing machine (5000 lb) which corresponds to about 900 psi for the size of this specimen. No mechanical deterioration of any kind was observed on the coated specimens during and after leaching, however small amounts of water were soaked through or into the coating. This gain of weight was about 1.46% for specimens coated with PVC after 60 days of exposure to solution and about 0.60% for specimen coated with PE/PB after 30 days of exposure to leaching solution.

Figure A-8 presents the cross section of a sodium chloride specimen cemented with 5% PB resin and coated with PE/PB coat after it has been leached a dense and strong coating encompasses the cemented sodium chloride core.

Table A-6 presents the recorded changes of pH, electrical conductance and concentration of sodium in the solution during the entire leaching period. From the uncoated specimens sodium chloride diffused into the solution very quickly, but from the coated specimens very slowly. The PE/PB coating was superior to the PVC coating in preventing the diffusion of sodium chloride.

TABLE A-4. MECHANICAL PROPERTIES OF SODIUM CHLORIDE COMPACTS CEMENTED WITH POLYBUTADIENE RESIN, UNCOATED, BEFORE LEACHING<sup>a</sup>

		Mecha	anical Propert	ies
Exp. No.	Specimen Designation	Hardness	Compression Strength psi	Bulk Density g/cm <sup>3</sup>
1	Sodium chloride cemented with 2% PB resin, uncoated	45	420	1.34
2	Sodium chloride cemented with 3% PB resin, uncoated	57	1230	1.40
3	Sodium chloride cemented with 4% PB resin, uncoated	59	1020	1.40
4	Sodium chloride cemented with 5% PB resin, uncoated	60	975	1.37

<sup>&</sup>lt;sup>a</sup> After leaching in water the specimens became soft and spongy and no measurements were possible.

TABLE A-5. MECHANICAL PROPERTIES OF SODIUM CHLORIDE SPECIMENS CEMENTED WITH POLYBUTADIENE RESIN AND COATED, AFTER LEACHING IN WATER

		Mecha	ınical Properti	es
Exp.	Specimen Designation	Hardness	Compression Strength psi	Bulk Density g/cm <sup>3</sup>
5	Sodium chloride cemented with 5% PB resin and coated with PVC	<b>5</b> 5	291 <sup>a</sup>	1.38
30	Sodium chloride cemented with 5% PB resin and coated with PE/PB system	30	>>900 <sup>b</sup>	1.36

Parallel specimen before leaching exhibited compression strength 714 psi, bulk density 1.24 g/cm<sup>3</sup> and hardness 55.

Before and after leaching the compression strength of this specimen exceeded the range of the testing machine, i.e., about 900 psi for its size.

TABLE A-6. pH, ELECTRICAL CONDUCTANCE AND CONCENTRATION OF SODIUM IN WATER DURING LEACHING OF SODIUM CHLORIDE SPECIMENS CEMENTED WITH POLYBUTADIENE RESIN (PB)

2						3	Days of Leaching	ching			
	Specimen Designation	Property	0		2	4	∞.	15	22	30	3
·	Sodium chloride cemented with 2% PB uncoated	pH A pumhos/cm Conc Na ppm	13.2	8.5 2.5 x 10 <sup>3</sup> 20300	X X 20706	9.5 141 x 103 24700	9.1 169 x 10 <sup>3</sup> 29200		9.0 9.0 8.6 179 x 10 <sup>3</sup> 179 x 10 <sup>3</sup> 188 x 10 <sup>3</sup> 30100 31360 32800	8.6 188 x 10 <sup>3</sup> 32800	8.8 94 x 103 54300
8	Sodium chloride cemented with 3% PB uncoated	pH. A particos/car Conc Na ppm	13.2	9.5 80 x 10 <sup>3</sup> 11400	x x 13200	9.4 133 × 10 <sup>3</sup> 14900	9.0 113 × 103 15100		9.0 8.8 8.7 141 x 103 151 x 19100 19100	8.7 151 × 103 30400	8.6 56 x 10 <sup>3</sup> 39800
ю	Sodium chloride cament with 4% PB uncoated	pH A pathos/cm Conc Na pom	13.2	9.8 80 x 10 <sup>3</sup> 11400	x X 12900	9.1 136 × 10 <sup>3</sup> 15200	8.8 169 × 10 <sup>3</sup> 22600	9.1 179 x 103 34400	8.8 9.1 8.9 8.9 8.9 169 x 10 <sup>3</sup> 179 x 10 <sup>3</sup> 188 x 10 <sup>3</sup> 113 x 22600 34400 35100 3960	8.9 113 x 103 39800	8.6 66 x 103 68400
4	Sodium chloride comented with 5% PB uncoated	ρΗ λ μπηλος cm Conc Na ppm	13.2	9.6 9.4 x 10 <sup>3</sup> 11600	x X 12500	9.5 164 x 103 23600	8.9 160 × 103 29300	9.2 160 x 10 <sup>3</sup> 29800	9.5 8.9 9.2 8.9 8.9 8.8 8.8 164 x 103 160 x 103 169 x 23600 29800 30200 30200	8.8 169 x 10 <sup>3</sup>	103 103 × 10 <sup>3</sup> 35300
2	Sodium chloride cemented with 5% PB and coated with PVC	pH λ μmhos/cm Conc Na ppm	13.2	6.6 310 70	××8	6.5 640 152	6.3 1.1 x 10 <sup>3</sup> 1.	6.8 20 × 50	10 <sup>3</sup> 2.8 × 10 <sup>3</sup>	4.7 x 10 <sup>3</sup>	8.5 6.6 x 10 <sup>3</sup>
R	Sodium chloride cemented with 5% PB and coated with PE/PB system	pH ) umhos/cm Conc Na ppm	13.2	6.8	×××	×××	5.6 141 4.25	5.6 94 5.00	×××	4.7 46 5.10	:

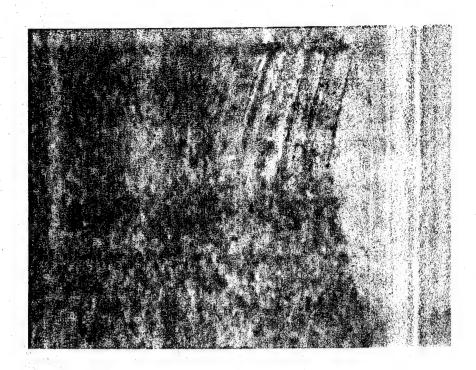


Figure A-8. Interface Boundary Between Cemented Sodium Chloride Compact and PE/PB Coat. (Magnification 4X)

The solutions resulting from leaching the uncoated specimens became alkaline. This may be the result of a faster diffusion rate for sodium ion than for chloride ion, there may be some chloride retention capacity of the cementing PB resin. After about 4 days of leaching, the pH of the solution, which exceeded 9, started to drop slowly. The solution resulting from leaching the specimen coated with PVC followed generally the same pattern with regard to the change of pH, but it took about a month to reach the pH level of 9, undoubtedly due to the reduced diffusion rate through the coating barrier. The change of pH of the solution resulting from leaching the specimen coated with PE/PB system was quite different, after few days of leaching the pH shifted in the acidic direction.

The electrical conductance of the solutions grew rapidly at the beginning of the leaching. After some time the conductance leveled off and even started to drop.

Table A-7 presents the calculated diffusion rates of sodium ions into the solution (grams/day/ $m^2$ ) for different time intervals. For uncoated specimens the initial diffusion rate through the surface varied between 500 and 1000 grams/day/ $m^2$  at the beginning and dropped to the value below 50 grams/day/ $m^2$  after 30 days. The diffusion rate of sodium through the applied coatings were negligible. Particularly effective was the PE/PB coat. The initial diffusion rate of sodium ions through it was about  $1g/day/m^2$ .

Testing of Hazardous Simulant Compacts Cemented with Polybutadiene Resin Table A-8 presents the mechanical properties of hazardous simulant specimens cemented with 7% polybutadiene resin, both uncoated and coated, after exposure to leaching solution for a period of 60 days. In all tested solutions the specimens behaved satisfactorily, no disintegration of any kind was observed during the entire period of testing.

Table A-9 presents the recorded values of pH, electrical conductance and concentration of toxic elements in the leaching solutions during the test period. In the aqueous and acidic solutions (Solutions A and B) shift of pH towards alkalinity could be observed; pH changed little, if any, in the alkaline and simulated solutions (Solutions C and D). There was a substantial increase of the electrical conductance resulting from the leaching of the uncoated specimen and only small changes resulting from the leaching of the coated specimens.

Only arsenic and selenium diffused into the solution in significant amounts from the uncoated specimen leached in water. After 60 days of leaching cadmium was found in concentrations below 3 ppm. Other elements were not detected at all or appeared only in trace amounts.

The cemented and coated hazardous simulant specimens exhibited generally satisfactory leaching resistance with regard to all tested elements except selenium and mercury. Relatively high concentrations of selenium were found in the alkaline leaching solution (Solution C) and of mercury in the simulated leachate solution (Solution D).

TABLE A-7. AVERAGE RATE OF DIFFUSION OF SODIUM IONS FROM SODIUM CHLORIDE COMPACTS CEMENTED WITH PB RESIN INTO WATER

	200	a washing a		il like					
Exp.#	Specimen Designation		Average R	ate of Di	ffusion g/	day/m <sup>2</sup> Bet	Average Rate of Diffusion g/day/m <sup>2</sup> Between Days of Leaching	f Leaching	
		0 - 1	1-2	2 - 4	4 - 8	8 -15	15 - 22	22 - 30	30 - 60
	Sodium chloride cemented with 2% PB uncoated	286	22	96	54	2.9	8.3	9.1	35
~ 1	Sodium chloride cemented with 3% PB uncoated	263	68	4	23	28	1	ı	15
ო .38	Sodium chloride cemented with 4% PB uncoated	533		75	28	79	4.7	27	44
4	Sodium chloride cemented with 5% PB uncoated	521	42	251	63	3.5	 	ŗ.	7.7
ഹ	Sodium chloride cemented with 5% PB and coated with PVC	3.0	0.86	1.34	0.02	0.38	0.53	1.28	0.31
30	Sodium chloride cemented with 5% PB and coated with PE/PB system	0.67			4.0	0.38		0.04	

TABLE A-8. MECHANICAL PROPERTIES OF HAZARDOUS SIMULANT SPECIMENS CEMENTED WITH 7% PB RESIN FOLLOWING LEACHING IN DIFFERENT SOLUTIONS

			Mecha	Mechanical Properties	ties
Exp. No.	Specimen Designation	Leaching Solution	Hardness	Comp. Strength psi	Bulk Density g/cc
9	Cemented, uncoated	A		211	1.76
7	Cemented, coated with PVC	¥		333	1.75
œ	As above	æ	35	537	1.63
თ	As above	U	30	141	1.54
10	As above	0	40	268	1.55

TABLE A-9. pH, ELECTRICAL CONDUCTANCE AND CONCENTRATION OF TOXIC ELEMENTS IN THE LEACHING SOLUTIONS OF HAZARDOUS SIMULANT SPECIMENS CEMENTED WITH 7% PB RESIN

						Đ	ays of	Leachin	g .				D. I. Watera	D. I. Water With Uncemented	
Exp. No.	Specimen Designation	Leaching Solution	Property	0	1	2	4	8	15	22	30	60	No Specimen 60 Days	Wasteb 60 Days	
			p∺	6.3	6.8	×	6.7	6.8	6.9	7.5	7.5	7.8	6.7	9.4	
	•		λ.umhos/cm	13.2	160	×	254	420	611	790	941	941	263	1790	
			conc.As ppm	×	10.5	15.2	23.0	31.3	27.5	27.9	31.4	118	a	420	
6	Cemented	A	conc.Hg ppm	×	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	5.1	
· .	Uncoated		conc.Se ppm	×	33.5	×	×	167.6	165.7	×	380	450	0		
			" Cd "	×	1.83	×	×	3.10	3.16	×	3.20	2.55	0	6.20	
	+ 1, - v		" Cr "	ж	0.00	×	×	0.02	0.00	×	0.00	0.00	0	0.27	
			н Pb ч	×	0.03	×	×	0.15	0.10	×	6.05	0.80	0	16.90	
			pM	6.3	6.4	×	6.3	6.4	6.4	7.6	8.1	7.9	6.7	9.4	
	-		λ.μmhos/cm	13.2	29.2	×	27.3	12.2	44.2	56.5	141	141	282	1790	
	Cemented A			conc. As ppm	×	0.0	0.0	0.0	0.0	1.0	1.1	0.0	0.0	0	420
		conc. Hg ppm	×	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	6.1		
	Coated	conc. Se pom	×	0.4	×	x	1.9	2.6	×	2.6	2.6	0			
	With Fig.	WITH PVC		conc. Cd ppm	×	0.03	×	×	0.07	0.11	×	0.05	0.14	0	6.20
			conc. Cr ppm	×	0.00	×	×	0.01	0.00	×	0.01	0.00	0	0.27	
			conc. Pb ppm	×	0.02	×	×	0.03	0.02	×	0.09	0.10	0	16.90	
			pH	3.8	4.1	×	4.2	4.2	4.2	4.5	4.6	5.2	х	×	
	Cerrenteo	В	λ <sub>s</sub> μ mhos/cm	56.5	74.2	×	75.5	49	65.9	96.0	179	179	x	×	
8 .	Coated		conc. As ppm	×	0.0	×	×	0.0	8.0	X	0.0	0.0	×	×	
	With PVC		conc. Se ppm	X	4.5	×	×	0.0	3.0	x	2.8	2.8	x	×	
			pH	10.2	10.1	×	10.0	10.0	9.9	10.1	9.9	10.0	×	×	
9	Cemented and	С	λ,μmhos/cm	21.6 ×103	20.7 x103	×	18.7 x103	21.6 x103	18.8 x103	19.8 x10 <sup>3</sup>	19.8 x103	18.8 x103	×	Х.	
	Coated With PVC		conc. Se pom		5.6	×	×	8.4	×	×	8.2	8.2	×	×	
•			conc. Cr ppm	}	0.00	×	×	0.00	×	x	0.00	0.00	х	×	
			pH	5.3	5.3	×	5.3	5.4	5.2	5.4	5.3	5.5	×	×	
			λ.umhos/cm	24.5	24.5	ж	24.5 ×10 <sup>3</sup>	24.5 x103	23.5 x103	23.5 x10 <sup>3</sup>	23.5 x10 <sup>3</sup>	19.8	х	x	
10	Comented and	D		x103	x103				1	1		x103	×	x	
	Coated With PVC		conc. As ppm		0.0	×	×	0.0	0.0	×	0.5	0.0	×	х	
			conc. Hg ppm		0.0	×	×	0.0	0.5	×	2.0	5.4	×		
	4		conc Se ppm	X	0.0	×	×	1 0.0	0.0	×	10.0	3.3			

Reference (DI - detonized water)
 150g of hazardous waste dispersed in 750 ml water.

Figures A-9, A-10, and A-11 show the interface boundaries between the cemented waste cores and the PVC coatings for specimens leached in acidic, alkaline and simulated leachate solutions.

Some distortion occurred on the interface boundary in the alkaline solution (Figure A-10), but none in the acidic or leachate solution. The alkaline environment therefore appeared to represent the most aggressive condition among the tested solutions.

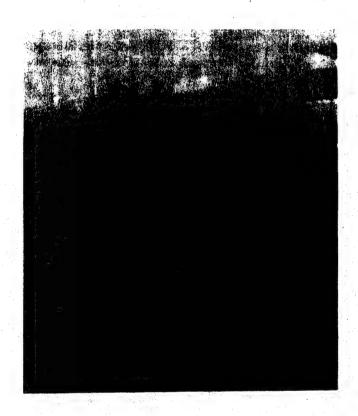


Figure A-9. Interface Boundary Between the Hazardous Simulant Core Cemented with 7% PB Resin and Coated with PVC After 60 Days of Leaching in Acidic Solution (Magnification 6X)

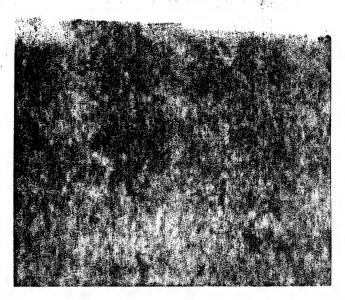


Figure A-10. Interface Boundary Between the Solid Waste Core Cemented With 7% PB Resin and Coated with PVC After 60 Days of Leaching in Alkaline Solution (Magnification 6X)

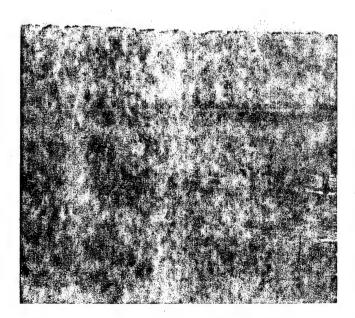


Figure A-11. Interface Boundary Between the Solid Waste Core Cemented With 7% PB Resin and PVC Coating After 60 Days of Leaching in Leachate Solution (Magnification 6X)

#### DISCUSSION OF RESULTS OF ENVIRONMENTAL TESTING

### Organic Cementation

Environmental testing revealed that polybutadiene resin is an adequate cementing agent for the consolidation of solids. To the extent of the testing performed both polyvinyl plastisol and polyethylene resin made jackets suitable for separation of the hazardous compounds embedded in the cemented core from the environment. Only traces of hazardous elements other than selenium appeared in the solutions following 60 days of leaching for specimens jacketed with polyvinyl chloride. Polyethylene resin modified with polybutadiene yielded jackets superior to the polyvinyl chloride suppressing diffusion of the sodium ions through the jacket; however, this coating, developed at the end of the research period, was not tested for penetration of heavy metal ions.

### APPENDIX B

Figures B-1 through B-8 are the calibration curves that were established for each leaching solution. They were determined by a standard addition analytical method. All concentration values for the cations in the leaching test solutions were calculated from these curves. These calibration curves are plotted through the average slope for each set of data points. The scatter of these points is indicated on the graphs. The mercury calibration data is listed, for all the solutions on one graph.

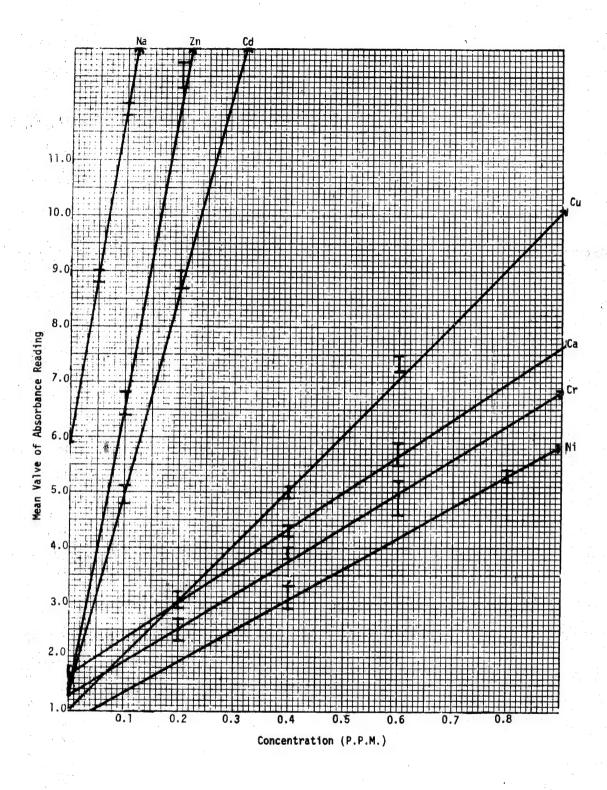


Figure B-1. Calibration Curves for the Cations in HCL and Distilled Water Solution

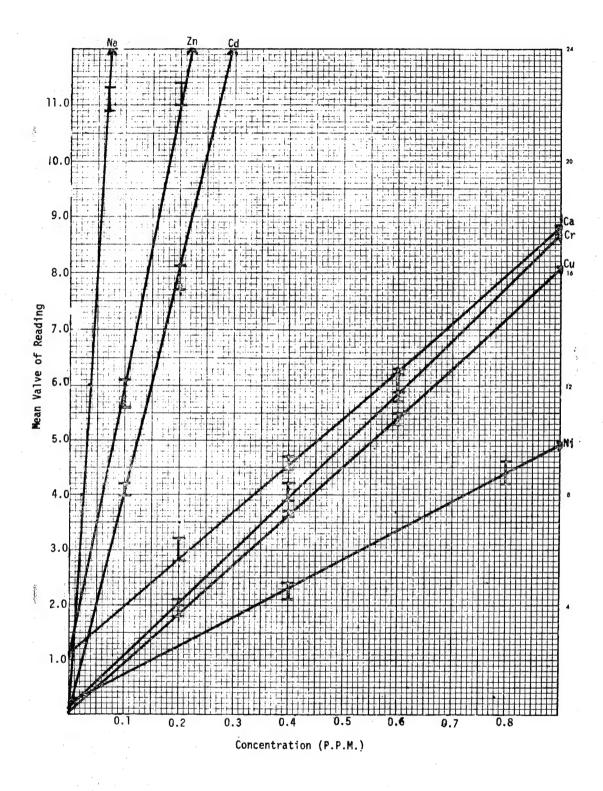


Figure B-2. Calibration Curves for the Cations in the Citric Acid Solution

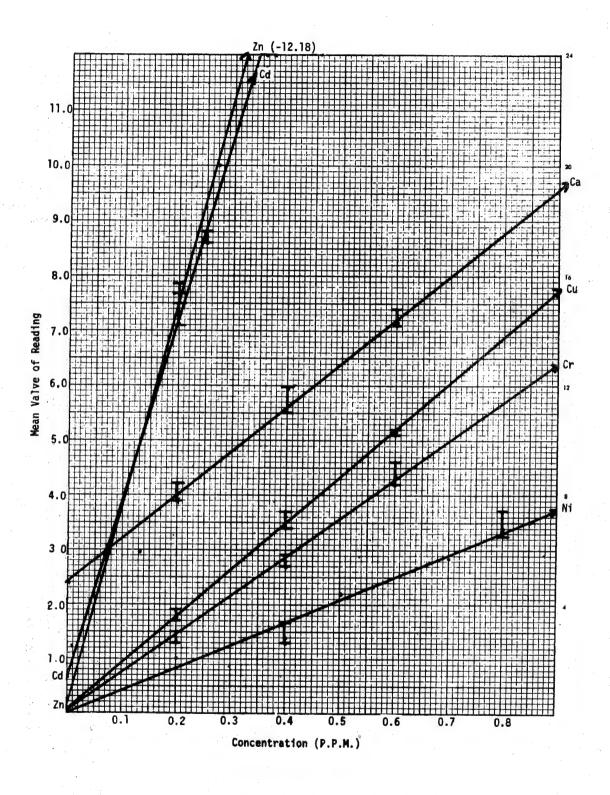


Figure B-3. Calibration Curves for Cations in NaOH Solution

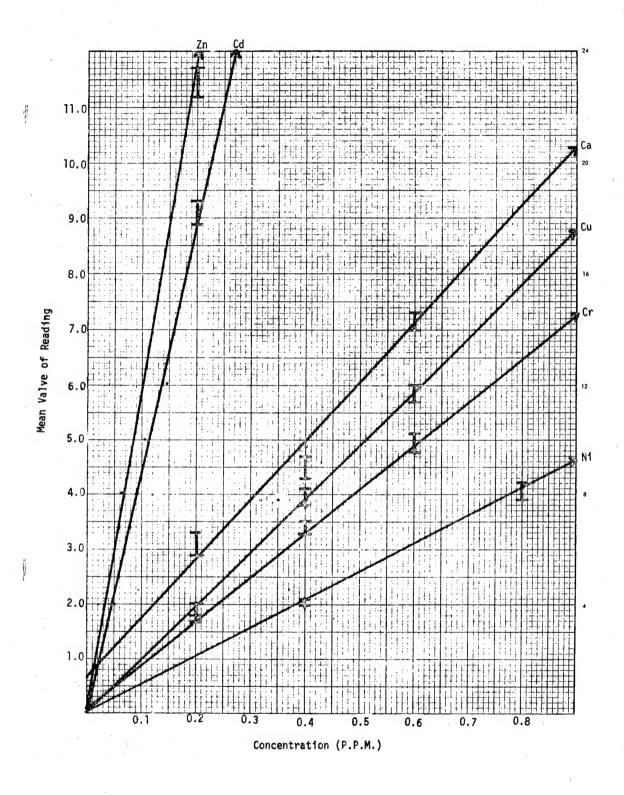


Figure B-4. Calibration Curves for Cations in NH<sub>4</sub>OH

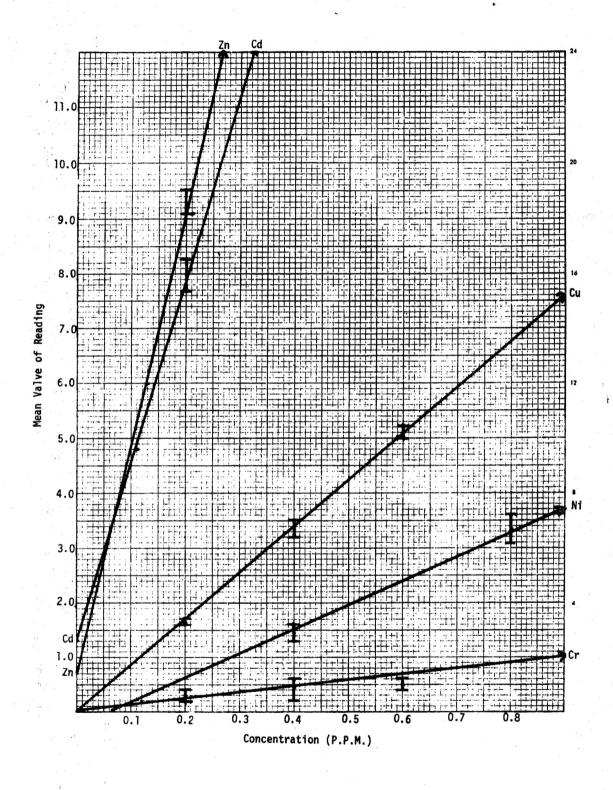


Figure B-5. Calibration Curves for Cations in Ocean Solution

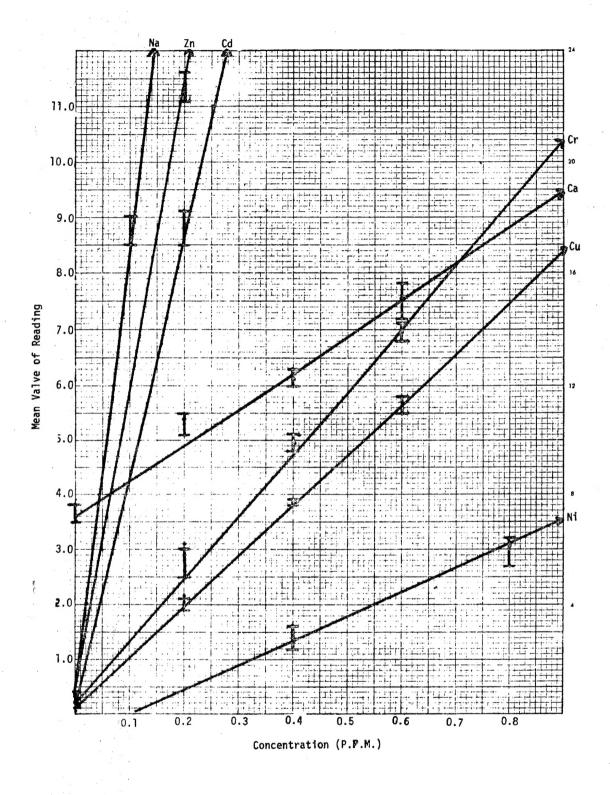


Figure B-6. Calibration Curve for the Cations in 10% Dioxane Solution

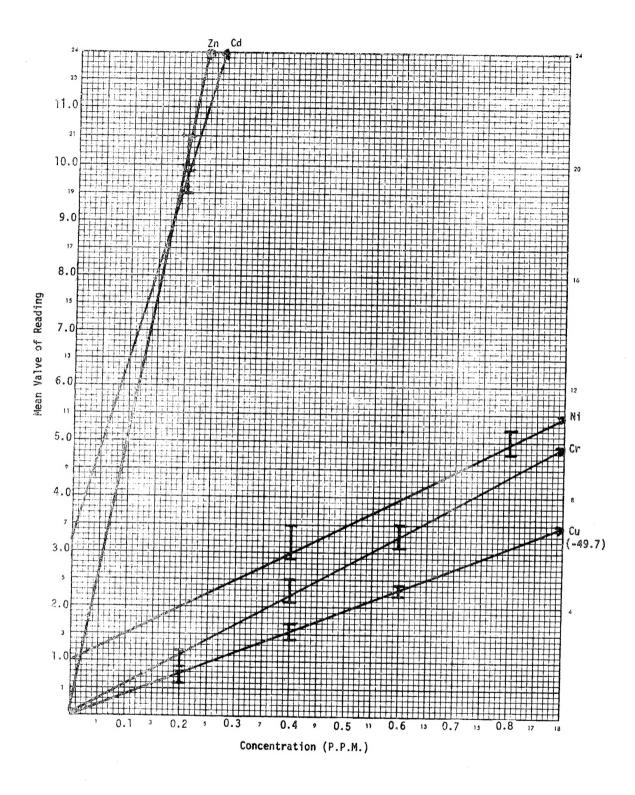


Figure B-7. Calibration Curve for the Cations in the Ammonium Sulfide Solution

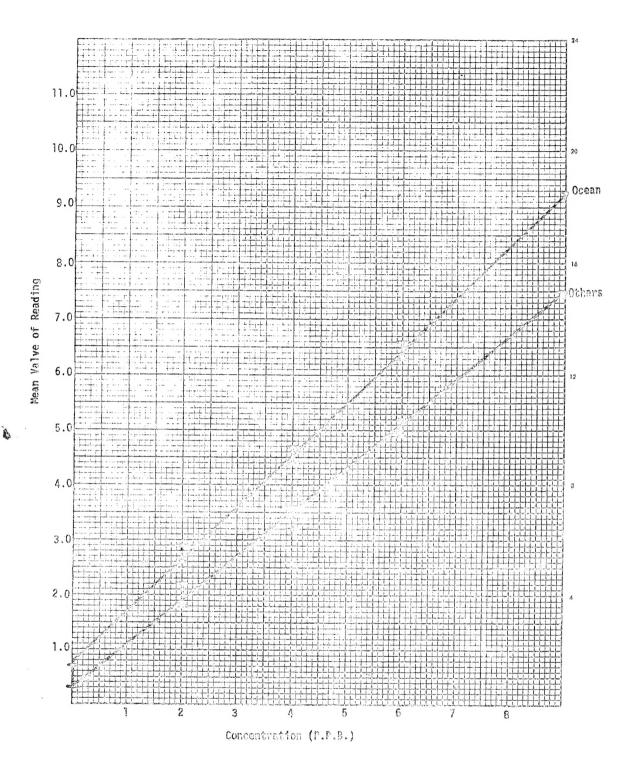


Figure B-8. Calibration Curves for Marcury in Leaching Solutions (Except Ammonium Sulfide)